

## Transparent and Flexible Field Electron Emitters Based on the Conical Nanocarbon Structures

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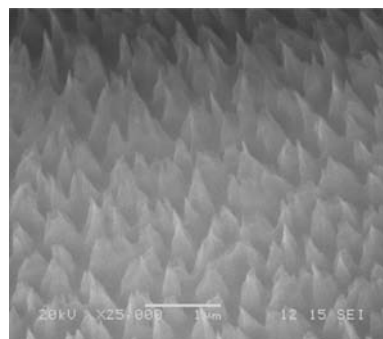
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The fabrication of conical nanocarbon structures (CNCSs) on a transparent and flexible nafion substrate, at room temperature using an ion irradiation technique, and their application toward field emission displays (FEDs) have been demonstrated. The main advantage of this technique is that CNCSs can be fabricated directly on the transparent substrate while retaining the transparency of the substrate. A scanning electron microscopy (SEM) image revealed that the sputtered surface was entirely covered with CNCSs with a calculated numerical density of  $\sim 6 \times 10^6 / \text{mm}^2$ . Such nafion based CNCSs have proved to be an effective electron emitter with turn-on and threshold fields of 6.1 and 9.5 V/ $\mu\text{m}$ , respectively. The field enhancement factor was estimated to be 1020 from the Fowler–Nordheim (F–N) plot. Thus the room temperature grown CNCSs, based on a transparent and flexible nafion substrate, would be very promising for future transparent and flexible (roll-up) FEDs.

For the past few years significant effort has been devoted to fabricating carbon nanotubes (CNTs) and carbon nanofibers (CNFs) based transparent and flexible electrodes due to their potential impact in a wide range of next generation optoelectronic fields. CNT based transparent and flexible devices have been demonstrated in numerous fields such as alternating current electroluminescence,<sup>1</sup> organic light-emitting diodes,<sup>2</sup> polymer solar cells,<sup>3</sup> transparent thin film transistors,<sup>4</sup> etc. Despite the success of these devices, the development of CNT/CNF based transparent field electron emitters still remains a challenge. In fact more recently, some researchers focused their attention on the fabrication of CNT/CNF based flexible FEDs.<sup>5–8</sup> In spite of producing the flexible FEDs, these approaches do not fabricate a transparent device. From the applications point of view the fabrication of both transparent and flexible FEDs rather than merely an opaque display could be of great interest.

Not only CNTs/CNFs but also conical nanocarbon structures (CNCSs) have been of substantial interest to the scientific communities because of their unique geometry and prospective application in various fields.<sup>9,10</sup> CNCSs have been produced by various techniques such as plasma enhanced hot filament chemical vapor deposition (HFCVD),<sup>11</sup> laser ablation,<sup>12</sup> and pyrolysis of organic compound.<sup>13</sup> However, for these methods growth temperatures higher than 750 °C are usually required. However, such a high growth temperature is a serious drawback which obstructs the growth of CNCSs on a flexible substrate. For the fabrication of CNCSs on a transparent and flexible substrate, a low temperature growth process, ideally at room temperature, is highly indispensable. In this regard, the ion irradiation method is considered to be very promising to fabricate CNCSs on a transparent and flexible substrate. This method was very useful for the fabrication of CNFs



**Figure 1.** SEM image of conical nanocarbon structures fabricated on the transparent and flexible nafion substrate.

at room temperature.<sup>14</sup> If the ion irradiation method produces CNCSs on a flexible and transparent substrate while retaining their transparency, the image will be visible from both the front and backside of the display. In this communication we tackled this subject very cautiously. For the first time we have investigated the previously unattainable fabrication of CNCS based transparent and flexible field emitter arrays.

CNCSs were prepared on a commercially available nafion substrate of size  $10 \times 10 \times 0.15 \text{ mm}^3$  by bombardment with  $\text{Ar}^+$  ions using a Kaufman type ion gun (ION TECH.INC.Ltd., model 3-1500-100FC). The incidence angle was normal to the surface, and irradiation was performed at room temperature for 30 s. The diameter and the energy of the ion beam employed were 6 cm and 600 eV, respectively. The basal and working pressures on the ion beam chamber were  $\sim 10^{-5}$  and  $5 \times 10^{-2}$  Pa, respectively. After sputtering, the morphology of CNCSs was carefully examined by scanning electron microscopy (SEM, JEOL; JEM-5600).

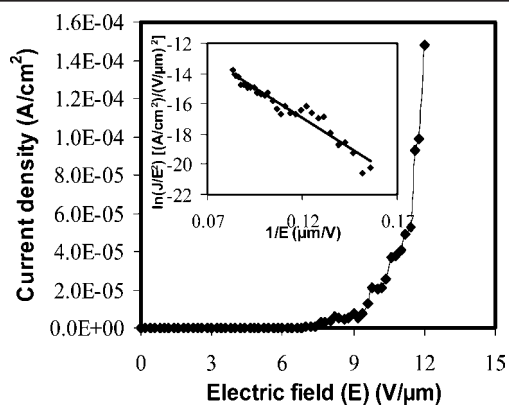
To measure the field electron emission (FEE) characteristics, a very thin layer of gold was coated onto the nafion based CNCSs substrate. FEE characteristics of the cathode thus prepared were measured for an applied voltage range of 0–1200 V under a parallel plate configuration at a typical working pressure of  $3.0 \times 10^{-4}$  Pa in an O-ring-shield glass chamber evacuated continuously by a turbo molecular pump. The cathode was separated 100  $\mu\text{m}$  from the anode by a spacer. The emission area was 0.1  $\text{cm}^2$ .

Figure 1 shows the scanning electron microscopy image of the sputtered surface of the transparent and flexible nafion substrate after coating with a very thin layer of gold.

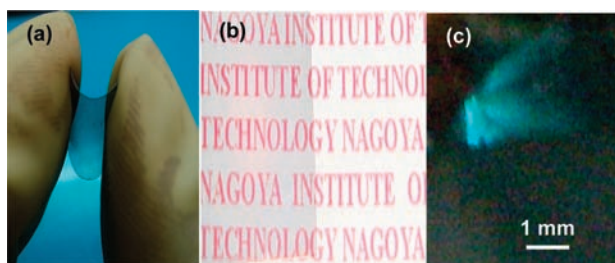
The SEM image clearly reveals that the entire surface was covered with uniformly distributed CNCSs. These CNCSs were 200 nm or larger in base diameter and a few hundred nanometers in length. The numerical density of the CNCSs was  $\sim 6 \times 10^6 /$

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**Figure 2.** Emission current density versus applied electric field curve for the conical nanocarbon structures. Inset shows the F–N plot.



**Figure 3.** Photograph showing (a) flexibility and (b) transparency of the substrate after coating a very thin layer of gold and (c) the green light emission from conical nanocarbon structures.

$\text{mm}^2$  as calculated from the micrograph. These CNCSs were pointed toward the ion beam pointing direction.

The emission current density versus electric field curve of the CNCSs fabricated on the transparent and flexible substrate is shown in Figure 2. The turn-on field corresponding to the current density of  $10 \text{ nA/cm}^2$  was  $6.1 \text{ V}/\mu\text{m}$ . Similarly, the threshold field, defined as the field required to extract a current density of  $10 \mu\text{A/cm}^2$ , was observed to be  $9.5 \text{ V}/\mu\text{m}$ . The inset of the Figure 2 shows the Fowler–Nordheim (F–N) plot. The straight line in the F–N plot indicates that the emission behavior follows the F–N model. The field enhancement factor,  $\beta$ , can be calculated using the F–N equation:  $J = A (\beta^2 E^2 / \varphi) \exp(-B\varphi^{3/2} / \beta E)$ , where  $J$  is the emission current density,  $\beta$  is the field enhancement factor,  $\varphi$  is the work function, and assuming the work functions of the CNCSs are similar to that of graphite ( $5.0 \text{ eV}$ ),  $E$  is the electric field,  $A$  and  $B$  are constant, and the value of  $B = 6.83 \times 10^9 \text{ eV}^{-3/2} \text{ Vm}^{-1}$ . The field enhancement factor,  $\beta$ , was found to be 1020.

The photographs of Figure 3a and 3b demonstrate the flexibility and transparency of the CNCSs based electron emitter, respectively. Thanks to the CNCSs' sizes being smaller than the wavelength of the visible light, the emitter maintained its transparency. To check its transparency, the CNCS based emitter was partially placed on a printed piece of paper, as explicitly shown in Figure 3b.

It was observed from the figure that the letters can be easily seen through the CNCS based emitter, except for a slight difference in clarity of the letters. This is due to the thin layer of gold coated on its surface. To observe the green light emission from this device, transparent zinc oxide deposited on indium tin oxide coated glass was used as a phosphor material. A very thin layer of gold was coated onto the transparent zinc oxide to make it conductive. However this phosphor material is only transparent but not flexible. A transparent as well as flexible phosphor material is still

commercially unavailable. This restricts the fabrication of transparent and flexible FEDs as well. Presently, we are trying to deposit phosphor materials onto a flexible and transparent substrate at room temperature. Eventually this could lead to the construction of transparent and flexible FEDs entirely. Figure 3c reveals the green light emission, from the transparent and flexible CNCS based device.

Recent studies indicate that carbon cones are effective electron emitters with a low turn-on and threshold field.<sup>11,15</sup> However, the carbon nanocone based flexible and transparent field emitter still remains unexplored. Recently, Zhao et al. showed that the carbon nanocones are excellent emitters with a turn-on field of  $3.2 \text{ V}/\mu\text{m}$ , and the emission current density from the carbon nanocones was observed to be as high as  $108 \mu\text{A/cm}^2$  at a field of  $5.8 \text{ V}/\mu\text{m}$ .<sup>15</sup> In our case, the turn-on field was found to be higher than the emission characteristics of carbon cones observed by the Zhao group. The sputter induced CNCSs on the nafion substrate could therefore be an enticing alternative to CNTs/CNFs as a field electron emission source for transparent and flexible FEDs.

In summary, we first demonstrated the room temperature grown CNCS based transparent and flexible field electron emitters. The demonstrated ion irradiation method is very helpful in constructing transparent and flexible field electron emitters without damaging the substrate. Also CNCSs can be conveniently fabricated at room temperature. Unlike other conventional methods, this method does not require any catalyst to fabricate CNCSs. This transparent and flexible emitter shows turn-on and threshold fields of  $6.1$  and  $9.5 \text{ V}/\mu\text{m}$ , respectively. Due to their unique geometry, the CNCS based FEDs could bring a revolution to the ubiquitous society because of its transparency, flexibility, light weight, and lower cost of production. Our next goal is to fabricate transparent and flexible phosphor material. The effort is underway and hopefully will be discussed in our forthcoming paper.

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