Patterned growth of carbon nanotubes on borosilicate glass

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Abstract.
We demonstrate the possibility of growing patterned carbon nanotube films on SnO_2:F-coated borosilicate glass by thermal CVD of acetylene at 630°C. The films showed slightly inferior field emission properties as compared to patterned films deposited on Si substrates.

Field emission has emerged as one of the most promising applications for carbon-based films, as attested by an increasing effort from researchers all over the world. In particular, carbon nanotube emitters [1] are purported to be ideal candidates for the next generation of field emission flat panel displays [2]. One critical issue at present is a better control of the growth, and in particular the realization of nanotube films deposited on glass substrates, which are the substrate of choice for display applications.

The first displays were realized by applying a nanotube-epoxy mixture onto a structured glass substrate and subsequent curing and activation [2]. Researchers aim now to deposit the nanotubes in a patterned way on glass by chemical vapor deposition (CVD) techniques. One hurdle is the temperature used for the growth, as borosilicate glass cannot sustain more than 650°C. Up-to-now, nanotubes were deposited by CVD on glass but only with the assistance of a plasma or a hot filament [3]. We demonstrate in this contribution that nanotubes can be grown on glass at temperatures below 650°C by simple thermal CVD.

Borosilicate glass, both as received and coated with a conductive SnO_2:F layer, were used as substrates. The catalyst was delivered onto the substrate by microcontact printing (μCP), a soft lithographic technique [4] [see Fig. 1(a)]. μCP involves loading a structured polymeric stamp, obtained by curing an elastomer on photoresist patterns deposited on a Si wafer, with a catalytic solution (the "ink"). The ink forms a polymerized gel on the stamp, which is then transferred to the

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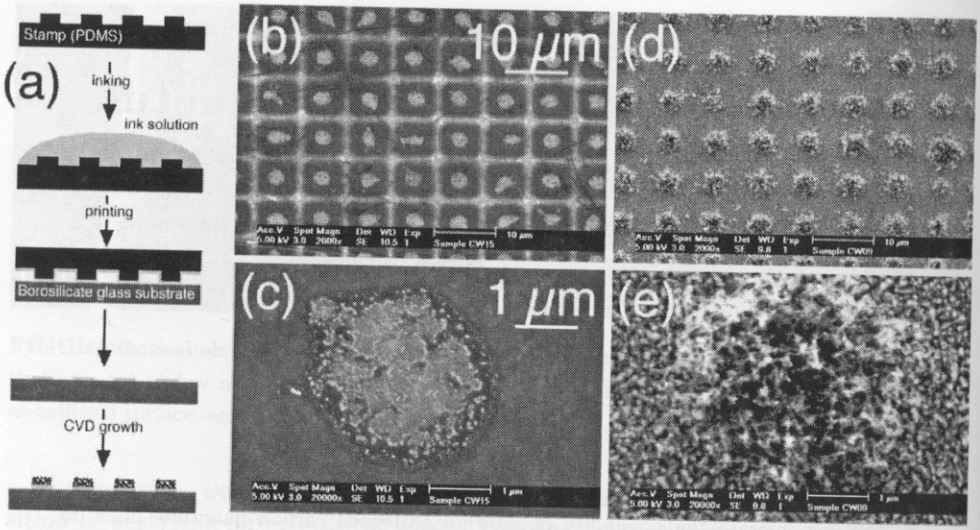

FIGURE 1. (a) Procedure for the patterned growth of carbon nanotubes on glass by μCP of catalysts. (b)-(e) SEM micrographs of the obtained films on borosilicate glass (b,c) and on SnO_2:F-coated borosilicate glass (d,e) with 200 mM Fe ink.

substrate by bringing stamp and substrate in conformal contact. μCP is a very simple and flexible method, and allows to structure a variety of surfaces (Si, glass, metallic surfaces...) with catalytic solutions.

In this contribution, the ink was an ethanolic solution of iron nitrate, $Fe(NO_3)_2{\cdot}9H_20$, with concentrations ranging from 50 to 300 mM, that was prepared 12 h before use [4]. The growth was carried out at 630°C in a tubular flow reactor at atmospheric pressure. The samples were annealed under N_2 flow for 10' before a 30' exposure to the hydrocarbon gas (1:4 mixture of C_2H_2:N_2). The procedure was completed by a 10' post-growth annealing under N_2.

Fig. 1(b,c) shows a sample obtained with a 200 mM Fe ink on glass. The pattern is readily visible (5×5 μm^2 squares separated by 5 μm), but very little growth is observed [some amorphous or graphitic carbon material can be discerned on Fig. 1(c)]. The results obtained on the SnO_2:F-coated substrates are far more convicing [Fig. 1(d,e)]: carbon nanotube "bushes" are present within the patterned areas and the growth is homogeneous over the whole surface. Note that as nanotube growth is not obtained below 630°C with our technique, the useful temperature range is quite limited.

The conductive SnO_2:F layer is thus not only useful to contact the nanotubes electrically, it seems also mandatory to obtain carbon nanotubes. We suspect that at the temperatures needed for the growth the metal diffuses rapidly into the glass, which greatly diminishes its catalytic activity and active surface. The SnO_2:F layer acts thus both as support and diffusion barrier. Note that the SnO_2:F layer

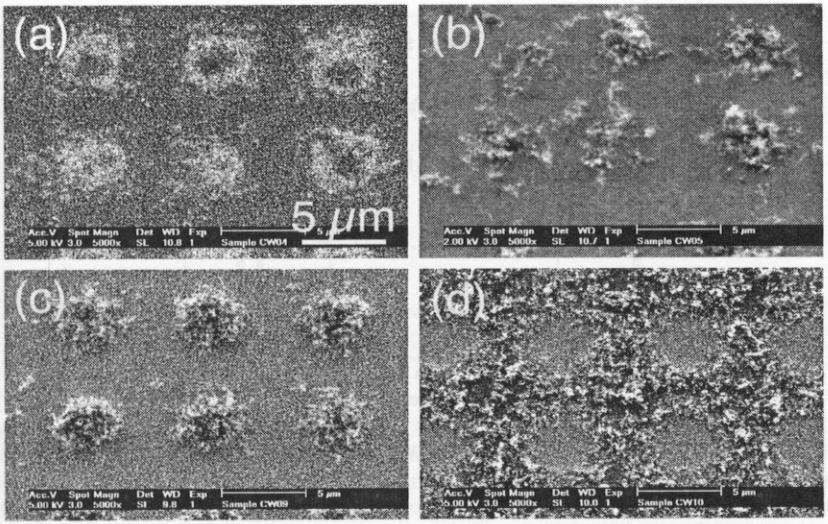

FIGURE 2. SEM micrographs of the obtained films on SnO_2:F-coated borosilicate glass with (a) 100 mM, (b) 150 mM, (c) 200 mM and (d) 300 mM Fe ink.

appears to be formed of an agglomeration of small particles, producing a rough surface [Fig. 1(e)].

Fig. 2 shows the influence of the catalyst concentration on the nanotube growth. As observed on Si [4,5], an increase of the concentration leads to higher nanotube densities inside the patterns. The concentrations needed to obtain a comparable density are, however, higher by a factor of 2 in the case of glass. This makes the realization of high density films problematic, as concentrated inks are more difficult to print than diluted ones. Fig. 2(d) shows the outcome for 300 mM: the growth is not confined to the patterns, and there is a significant proportion of other forms of carbon in the deposit. A concentration of 200 mM seems therefore to be an optimum for the substrate and catalyst used.

We also characterized the field emission performance of the obtained films. The substrates were loaded in a UHV chamber (base pressure 10^{-7} mbar), and the field emission was measured using a stainless steel sphere of 1 cm diameter as the counterelectrode. The distance between the electrodes was 125 μm. Two typical emission curves are shown in Fig. 3 for nanotube patterns grown on Si and on SnO_2:F-coated borosilicate glass. The films obtained on Si reach turn-on current densities of 10 μA cm^{-2} at fields of 4.2 V/μm, as compared to 5.1 V/μm for the film shown in Fig. 1(d,e). In fact, the films we obtained on glass were systematically less efficient emitters than those deposited on Si.

We suppose that most of the observed shortcomings (difficulty of growing films with a density comparable with those obtained on Si with the same catalyst, higher emission fields) are due to the nature of the conductive film. While it appears that

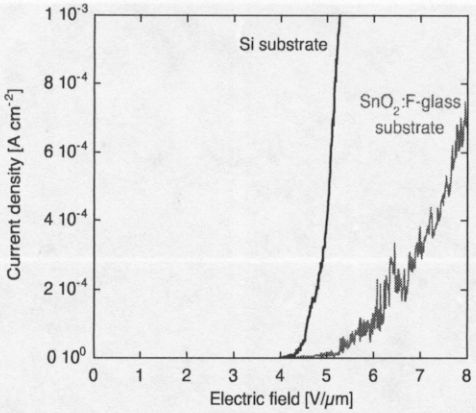

FIGURE 3. Field emission $I - V$ curves for patterned carbon nanotube films deposited on Si and SnO_2:F-coated borosilicate glass.

the SnO_2:F prevents diffusion of the catalyst into the glass, its roughness decreases the effective area that is in contact with the stamp during printing, leading to a smaller amount of transferred catalyst as compared to a flat surface. The use of Indium Tin Oxide (ITO) or of amorphous Silicon (a:Si) could probably lead to a significant enhancement of both growth and field emission properties. Another possibility would be to decrease the temperature to prevent the diffusion of the catalyst. This could achieved either by using another gas (such as CO), or by improving the catalyst (e.g., by adding other transitions metals such as Pd).

In conclusion, we have shown that it is possible to grow nanotube patterns on glass by thermal CVD at temperatures below 650°C. A conductive SnO_2:F layer was necessary to obtain nanotubes, probably because of diffusion of the metal catalyst in the bulk of the glass substrate at the tempertaures used for growth. The films showed slightly inferior field emission properties as compared to patterned films deposited on Si substrates.

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REFERENCES

1. Bonard, J.-M., et al., *Sol. St. Electron*, **45**, in press (2001).
2. Choi, W.B., et al., *Appl. Phys. Lett.*, **75**, 3129 (1999).
3. Ren, Z.F., et al., *Science*, **282**, 1105 (1998).
4. Kind, H., et al., *Adv. Mater.*, **11**, 1285 (1999).
5. Klinke, C., Bonard, J.-M., and Kern, K., *Catal. Lett.* (submitted).