

Carbon Nanotube Growth for Vias and Interconnects

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The continued scaling of device dimensions leads to the current density in interconnects exceeding the limit of copper ($\sim 3.10^6$ A/cm²) after the 16 nm node. Carbon nanotubes are one of few materials that can carry current densities of over 10^8 A/cm². They can also be grown in high aspect ratio holes, and do not need liners to isolate them from the surrounding materials. However, their quantum resistance of $h/4e^2$ per shell means that their resistance is higher than the copper equivalent, unless they can be paralleled in very high density $\sim 3.10^{13}$ cm⁻². CNT interconnects require four key properties; a high density, maximum growth temperature of 400C, growth on metal substrates, and high fraction of metallic tubes. However, nanotube density remains the key bottleneck. Over the last 5 years, Awano et al [1,2] have gradually increased the nanotube density, from $\sim 3.10^{10}$ cm⁻² to $\sim 10^{12}$ cm⁻² now.

This paper presents some results from an EC funded project to develop CNT interconnects involving partners Cambridge University, CEA Grenoble, Intel Ireland and EPFL Lausanne.

We have introduced new growth techniques to achieve a nanotube density of up to 5.10^{12} cm⁻². Our growth processes are developed from those used for high-density, vertically aligned CNT forests [3]. In the two best documented cases, Futaba et al [4] and Zhong et al [5] grew forests of density $5.3.10^{11}$ cm⁻² and 8.10^{11} cm⁻² respectively. The high density causes the vertical alignment, but it is still much lower than that required for Vias. In Futaba's case, the nanotubes had a mean diameter of 4 nm, the catalyst droplets had a mean diameter of 6 nm, and the forest was only 4% dense [4]. That is, the catalyst droplets cover only a small fraction of the available growth surface. Fig 1 shows how the nanotube density might be raised by a higher filling factor.

We are using two ways to increase CNT density - reduce the CNT diameter, or fill the growth surface with more catalyst nano-particles. In the standard catalytic chemical vapour deposition (CVD), there are three process steps; thin film catalyst deposition, annealing for catalyst restructuring, and then growth. The critical step is catalyst re-structuring [6], in which a thin film

catalyst (Fe, Co or Ni) on a support layer de-wets and forms a series of active nanoparticles (Fig 2b). We have modified the deposition and annealing steps to increase the CNT density to 2.10^{12} cm⁻² or over. Fig. 3(b) shows an AFM scan of the catalyst before growth for the new process. Growth occurs in atmospheric pressure diluted acetylene. Fig. 4 shows high resolution SEM images of the forest side for the normal process and that with the modified annealing step. Fig 5 high resolution TEM of the double-wall nanotubes, with average diameter 4.5 nm and density of 2.10^{12} cm⁻².

In separate experiments at CEA, a CNT density of 2.10^{12} cm⁻² was achieved for growth using Fe catalyst on AlCu alloy (0.5% Cu) at 580C. The CNT density is measured by three methods; directly by SEM images, by weight gain and measuring the CNT diameter and wall number by TEM, and finally by isopropanol wetting to measure the filling fraction. In a second method, cluster beam deposition is being studied to deposit Co catalyst.

We have also transferred growth to metallic substrates such as TiN and CoSi₂. Initially, this gives lower density forests, because catalyst de-wetting works less well in this case. However, pre-treatments such as oxygen plasmas can enhance the nucleation densities [7]. On the other hand, AlCu is found to support the highest nanotube density growth, and it is metallic, covered with an ultra-thin AlO_x layer due to oxidation by O₂ exposure either during specimen transfer, or by small background pressures of oxygen.

Growth in Via holes has been achieved. Catalyst is deposited down the holes in the SiO₂ dielectric [8]. Good hole filling is achieved, with nanotube densities inside the hole similar to that for blanket growth (Figs 6,7). Good yield is also achieved (Fig 8).

Finally, horizontal interconnects are also being developed. Here, high density growth is more difficult. Horizontal orientation is achieved in two ways, either by growth from catalyst deposited on a vertically oriented surface, or by vertical growth followed by flip down. To date, we have only achieved densities of 6.10^{10} cm⁻² of small diameter multiwalled tubes, using Fe as catalyst on CoSi₂ coated vertical surfaces.

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1. M Nihei, et al, Jpn J App Phys 44 1626 (2005)

2. Y Yamazaki et al, App Phys Exp 3 055002 (2010)
3. K Hata et al, Science 306 1362 (2004)
4. D N Futaba et al, J Phys Chem B 110 8035 (2006)
5. G Zhong et al, Carbon 44 2009 (2006)
6. S Hofmann et al, J App Phys 98 034308 (2005); M Cantoro et al, Nanolett 6 1107 (2006)
7. C Esconjauregui, et al, App Phys Let **95** 173115 (2009)
8. J Dijon et al, Diamond Related Mats 19 382 (2010)

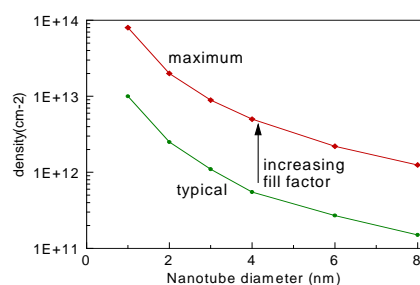


Fig 1. Nanotube density vs. nanotube diameter for catalyst utilisation as in [4], compared to maximum

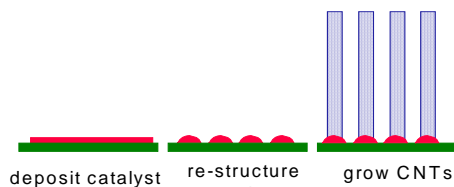


Fig. 2. Three step process to grow carbon nanotubes

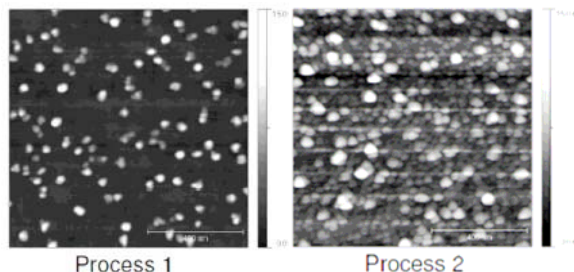


Fig. 3. AFM images of catalyst nanoparticles after step 2, for (a) normal process and (b) modified anneal process. Fe as catalyst and AlO_x as support layer

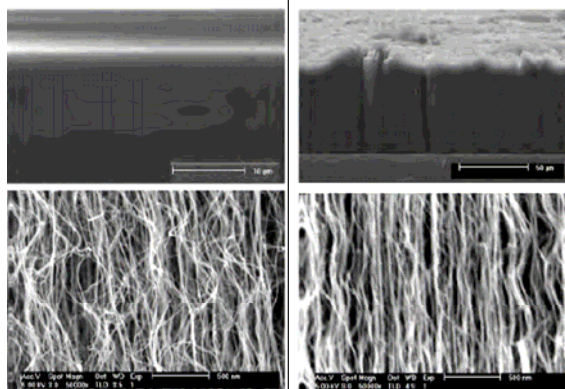


Fig 4. SEM images of the CNT forests, (a) for normal process, (b) after modified anneal

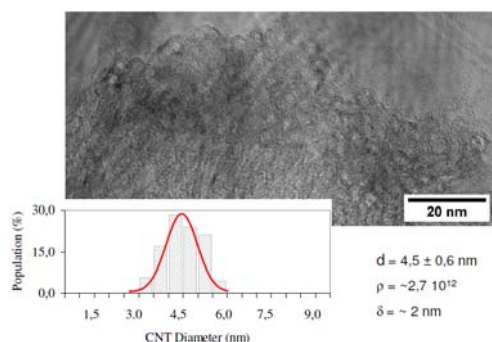


Fig. 5. High resolution TEM of the nanotubes after modified process, showing average diameter of 4.5 nm.

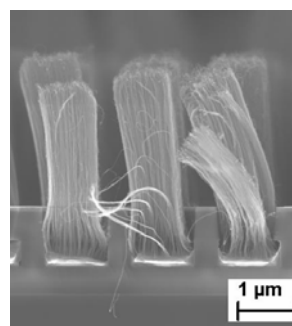


Fig. 6. High density grown nanotubes ($2.10^{12} \text{ cm}^{-2}$) in 1 μm Via hole.

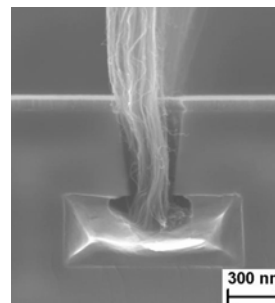


Fig. 7. High density nanotube growth in 250 nm Via hole.

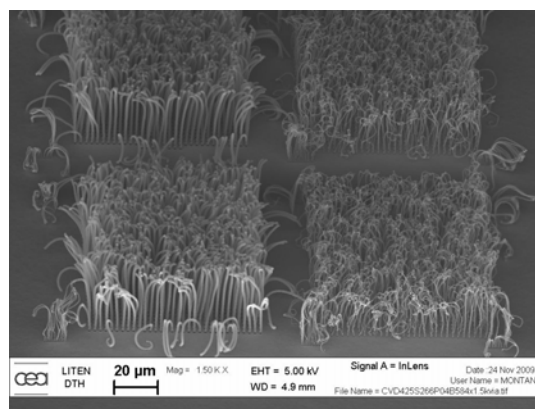


Fig. 8. Showing good yield of growth in arrays of 1000 vias of 1 μm and 500 nm.