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Highly Dense Carbon Nanotube Forests for Interconnect Applications

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The continued scaling of VLSI device dimensions means that the current densities carried by interconnects will soon exceed the limits of copper, ~6.10^6 A/cm^2 [1,2]. The only material able to carry higher current densities is sp^2 bonded carbon, either carbon nanotubes (CNTs) or graphene, which can carry of order 10^9 A/cm^2. However, these huge capacities are unusable unless we can produce CNTs with area densities of order $3x10^{13}$ cm^{-2} because they are one–dimensional conductors with a series quantum resistance. Achieving this density is non-trivial, as it corresponds to an inter-tube spacing of 2 nm, and CNT diameters are typically 1-2 nm. Here we present three methods which can give area densities of order $1.5x10^{13}$ cm^{-2}, close to this limit.

Fig. 1 summaries the state of the art of area density for standard 'super-growth' CNTs, as produced by Hata et al [3,4] or Zhong et al [5] who achieved only ~$6x10^{11}$ cm^{-2}. This compares with previous densities in Via structures of typically 10^{11} cm^{-2} until recently [6,7] It has been difficult to increase this area density. We plot here [8] curves for the theoretical dense limit for area density N vs. diameter of single wall nanotubes, d, N ~$1/d^2$.

There are two ways to increase the area density, either increase the packing fraction, or decrease the nanotube diameter.

In the chemical vapor deposition (CVD) of CNTs, the CNTs grow from catalyst nano-particles, one CNT for each nano-particle, and with the nanotube diameter roughly equal to that of the nano-particle. Now, the catalyst nano-particles are produced from catalyst thin films by a de-wetting process. This means that the nano-particle diameter is proportional to the initial thickness of the catalyst layer h, typically d~ 6h. It is difficult to reduce h much further, it is already well under 1 nm.

The first way to reduce h is to reduce the possibility of diffusion of the Fe catalyst into the underlying support layer, here Al_2O_3, by plasma oxidation and compaction [9]. This allows us to reduce catalyst thickness to 0.3-0.4 nm. The resulting nanotubes (SWNTs) have average diameters of 1.1 nm from high resolution transmission electron microscopy (HRTEM) images. This estimate is supported by Raman spectroscopy on the radial breathing modes.

The area density can be estimated by three ways, counting, liquid induced compaction and by weight gain. Weight gain is the more reliable for blanket samples. This involves measuring the weight gain, and the diameter and number of walls from TEM to get the mass per unit length of one CNT, which then gives the area density.

From this, we estimate an area density of $1.5x10^{13}$ cm^{-2} for the forest of diameter 1.1 nm. The mass density of this is 0.3 g/cm^3, six times higher than in super-growth.

The second method is cyclic deposition. This uses cyclic deposition to increase the nucleus density [10]. But the tubes are still double walled and the diameter is 2.4 nm. We previously estimated area density by liquid induced compaction. We now use the more reliable method of weight gain. The mass density is measured as 0.5-0.6 gm/cm^3, extremely high, and corresponding to an area density also of ~$1.3x10^{13}$ cm^{-2}.

It is important to stop growth directly, not allow it to terminate, as this can result in a low density layer at the roots.

The third method follows the three-step plasma treatment method of Yamazaki et al [7]. We have repeated this process, checking optimization, and found it to be valid. Our steps are deposit the catalyst, use an Ar plasma to restructure the catalyst, use a short carbon plasma 15 s dc-plasma (1 W/cm^2, 3.5 mbar, 15-30 % C_2H_2, 200-400 C) to deposit a carbon layer to immobilize the catalyst nanoparticles, and then have CNT growth in 4-10% C_2H_2 at 490-650 C without plasma.

Whereas the original authors used SEM counting to estimate the area density, we used the more reliable weight gain method. In our case the average diameter is 4.8 nm (less than in original paper), the wall number is 2, and the mass density is 0.36 gm/cm^3 (see Fig 5). This gives an area density of $2x10^{12}$ cm^{-2} , and a wall density of $4x10^{12}$ cm^{12}.

We believe that combinations of these various processes will allow densities of 10^{14} cm^{-2} to be achieved, eventually. We are now studying conductive support layers such as TiO_2 or TiN to optimize the Via resistance.

References

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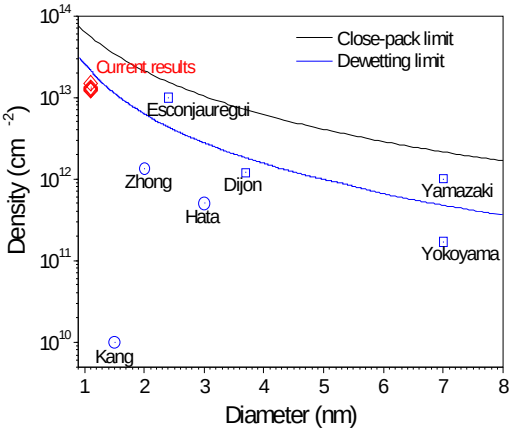

Fig. 1. Area density of vertically aligned carbon nanotube forests of various workers vs. CNT diameter.

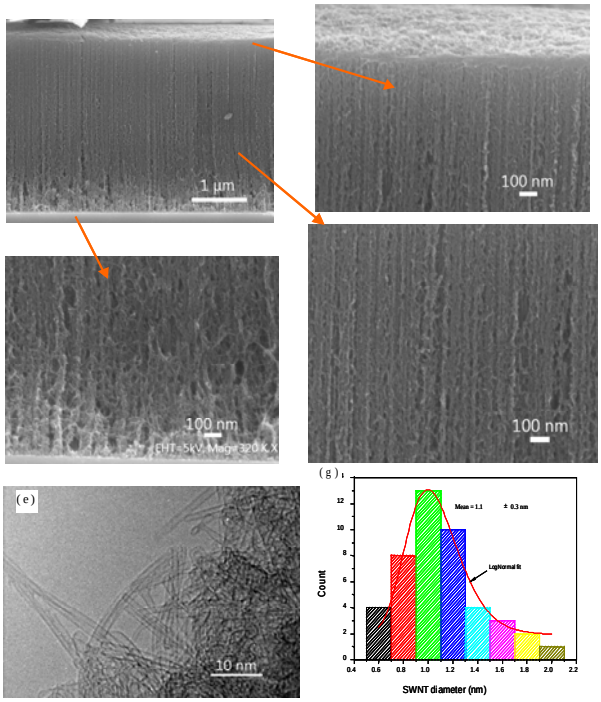

Fig. 2. SEM images, HTEM images, and diameter distribution for SWNTs grown on densified Al2O3 support layer.

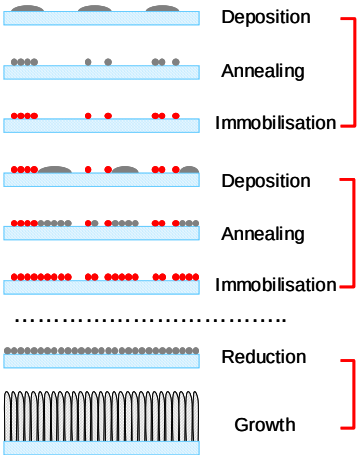

Fig. 3. Process flow for the cyclic growth method, to immobilise the catalyst

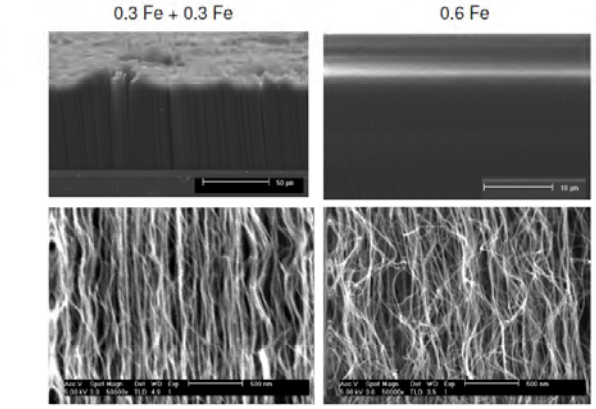

Fig. 4. TEM and SEM images of cyclic growth compared to standard single cycle growth.

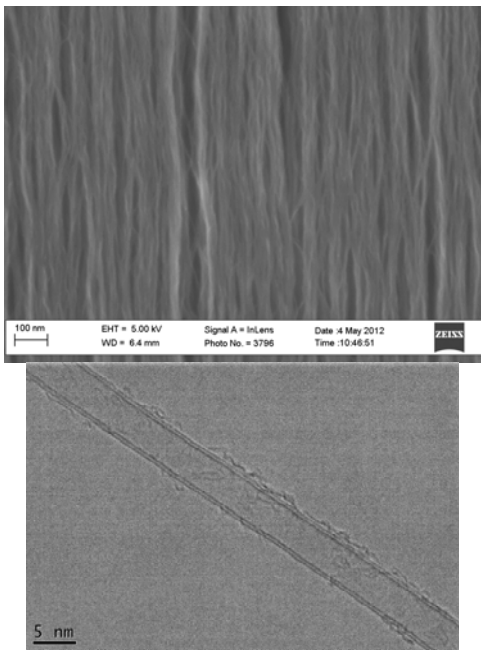

Fig. 5. SEM and TEM images of double wall CNTs resulting from the 3-step carburisation method.