

Synthesis of diameter and chirality controlled CNTs in zeolites, and their integration on wafers.

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Despite the exceptional electrical characteristics of CNTs, doubts have arisen concerning their real technological integration in electrical devices. The requirements for carbon nanotubes (CNT), to replace copper in future interconnects, as mentioned in the ITRS roadmap, are indeed very strict: essentially defect-free metallic aligned Ts, oriented on substrates in high densities (0.1-0.3 CNT/nm²) at specific locations (1).

Control of the numbers of graphitic layers is state-of-the-art. While in the 1990s, multi-walled carbon nanotubes (MWCNT) composed of several graphitic layers were synthesized, the focus was shifted toward nanotubes having a single graphene layer (SWCNT) and more recently synthesis efforts were extended to tubes with two graphene shells (DWCNT) (2).

Although progress has been made in controlling nanotube chirality and diameter during synthesis, no reliable synthesis procedure is available now that allows the production of aligned CNT of one specific type. Bulk synthesis procedures such as the pulsed laser vaporisation (PLV) and arc discharge methods provide mainly bundles of nanotubes with a broad distribution of tube diameters and chiralities (3). Chemical vapour deposition (CVD) procedure enables the growth of individual SWCNTs directly on flat substrates. Notable progress has been made towards controlling the SWCNT diameter by using well-defined and characterized nanoclusters as catalysts. These methods yield SWCNTs with diameters close to that of the individual metal particles formed upon chemical reduction of the precursor (4). The average tube diameter in SWCNT samples produced by the currently employed methods is around 1 nm. However, the density of the carbon nanotubes is orders of magnitude too low, and practically not useful. Smaller SWCNTs have been reported sporadically. The smallest tubes to date have a diameter of 0.3 nm. (5).

We here present the controlled synthesis of ultra-small diameter nanotubes (3 – 8 Å) in well-defined subnanometer sized confined space within zeolites. Zeolites are crystalline materials with a high density of pores with molecular dimensions. They generally find application as molecular sieves to separate molecules of different sizes. Depending on the zeolite type, the pores are aligned parallel, going from one side of the crystal to the other. The pores have uniform diameters, and are separated from each other by one to several M-O layers (with M = P, Si or Al), while the density of the pores equals the required CNT density for interconnect applications. It will be demonstrated that SWCNTs can be formed in the pores of such zeolite crystals. The synthesis simply implies a heat treatment of the zeolite crystal in inert atmosphere after filling the pores with a suitable

carbon source. The growth mechanism of the CNT is different from the classic CVD procedure, and is unique for zeolites. While no metal is required to catalyze the CNT formation, we envision the presence of Brønsted acidity is crucial. Notably low temperatures (< 800 K) are sufficient to accommodate the growth of SWCNT inside the pores of zeolites.

In most cases, the number of chiralities is limited due to a diameter control. As an example, small pore zeolites such as ALPO-5 (with AFI topology, see figure 1), with a pore diameter of 0.73 nm, allow the controlled synthesis of only three SWCNTs (6). Raman spectroscopy, photoluminescence and X-ray diffraction (with Rietveld refinement) show the presence of (3,3), (5,0) and (4,2) chiralities. Interestingly, their distribution can be influenced by the elemental composition of the zeolite.

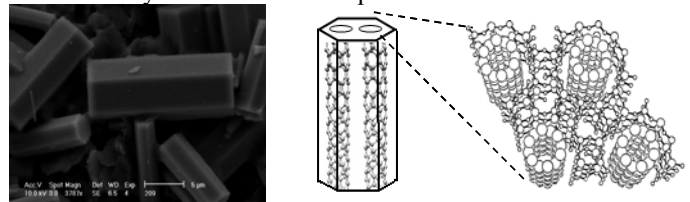


Figure 1. SEM image of ALPO-5 zeolite [left], with scheme of zeolite crystal with straight aligned parallel pores [middle] and detail of (5,0) SWCNT occluded in the zeolite pore [right].

Different zeolite topologies are explored, and evaluated for nanotube synthesis. Further insights into the growth mechanism of occluded ultra-small diameter nanotubes will be presented, leading to a preferential synthesis of metallic CNTs in the molecular sieves. Next to SWCNTs, the selective synthesis of metallic DWCNT in zeolite pores will be demonstrated as well. In addition to Raman, photoluminescence and X-ray diffraction, conductivity and magnetism measurements of the CNT filled zeolites will be explained in detail.

Next to the controlled synthesis of CNTs, the presentation includes a new process to selectively integrate the synthesis of zeolite crystals on chips (Fig. 2). Both horizontal and vertical growth of zeolite (and thus CNTs) will be demonstrated. As temperatures below 800K are envisioned for the both zeolite and nanotube synthesis, the processing is compatible with current CMOS technology platform, while the obtained CNT densities are in accordance with ITRS standards for future interconnects, the confined zeolite-assisted CNT growth is a viable pathway for integration of CNTs in the chip of the future.

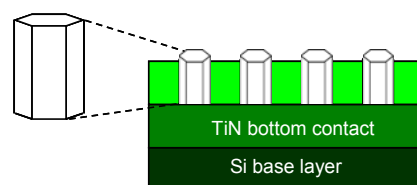


Figure 2. Integration of zeolite on a patterned chip.

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