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Plasma-Enhanced Chemical Vapor Deposition in a Transmission Electron Microscope?

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In plasma-enhanced chemical vapor deposition (PECVD), reactive species generated by the plasma have the effect, among others, of changing the surface energies of the growing materials, which allows one to prepare objects that would not stabilize otherwise. Here, we use this property to stabilize Sn droplets used as catalysts in the growth of Si nanowires (SiNWs) with the vapor-liquid-solid (VLS) method [1]. However, the conditions necessary to ignite a plasma are not compatible with transmission electron microscopy (TEM), so that adapting the growth conditions of a PECVD reactor to *in-situ* TEM is hardly imaginable, hence the question mark in our title.

The TEM equipment we use is the environmental transmission electron microscope "NanoMAX", a modified Thermo Fisher Titan ETEM. To circumvent the incompatibility between PECVD and TEM, we implemented, on the H_2 line of that ETEM, an electron-cyclotron-resonance plasma source (Aurawave from SAIREM), to remotely generate the H atoms necessary for the growth. Our *in situ* observations (Fig. 1) clearly show that, without the supply of hydrogen atoms ("plasma OFF", in Fig. 1), the liquid Sn at the top of NWs is unstable (because Sn naturally wets Si surface) so that no growth is allowed, whereas in the presence of H atoms generated by the plasma, the Si surface energies are drastically lowered [2]; the Sn droplet stabilizes and can be used by the VLS mechanism of growth [3].

Moreover, we have recently found [4] that the addition of Cu to Sn, to make Cu-Sn bi-catalysts, allows one to reduce the size of the liquid nanoparticles below 10 nm, which appears to be a necessary condition for obtaining SiNWs with the hexagonal 2H polytype [2,4,5] (Fig. 2), a metastable structure that would have interesting optical properties [6]. Thanks to our unique setting, we have been able to obtain Sn-Cu-catalyzed SiNWs *in-situ*, with 2H regions [7]. The talk presents the effect on NW growth of switching the plasma on and off, and shows movies of the nucleation of the Si 2H metastable polytype recorded at atomic resolution [8].

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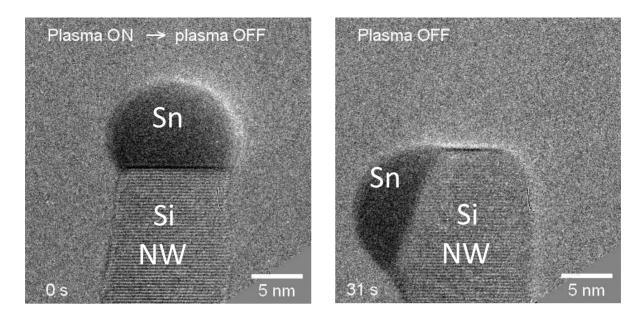


Figure 1. SiNW grown *in situ* in NanoMAX with Sn catalyst, at the moment of switching plasma off (0 s, left) and 31 s after plasma has been switched off (right).

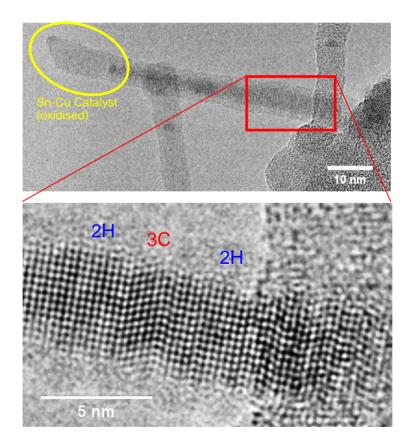


Figure 2. 2H SiNW obtained in a PECVD reactor [4], with a short 3C (cubic) domain.