ESRF	**Experiment title: Strain and composition of Silicon Nanowires, grown with gold catalyst, investigated by Grazing Incidence Diffraction Anomalous Fine Structure**	**Experiment number**: 02-01-819
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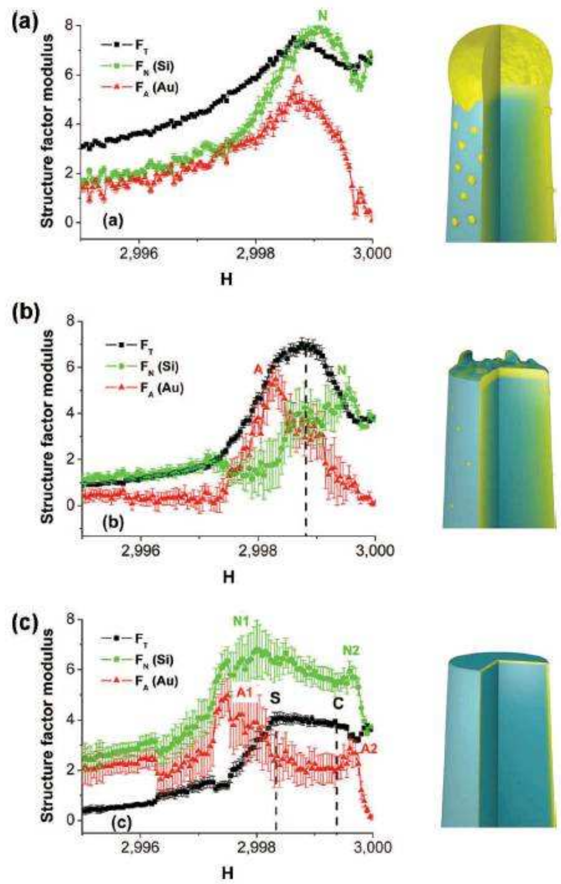
Report:

Silicon nanowires were grown by Gold catalysed Chemical Vapor Deposition in the Vapor Liquid Solid mode. In this experiment we use Grazing Incidence X-Ray Diffraction and Multiwavelength Anomalous Diffraction (MAD) to investigate the presence of gold and its effects on silicon nanowire strain after different chemical and physical treatments. We especially focus on the efficiency of the "thermal oxidation - oxide etching" cycle to remove the gold contamination.

The figure displays the results of MAD measurements performed on the three groups of samples A (as-grown), B (I-KI Gold Chemical Etching) and C (I-KI Gold Chemical Etching Thermal Oxidation HF Deoxidation) along with sketches illustrating the possible spatial distribution of the gold contamination we propose. Analysis of the diffraction intensity variation before and after the gold LIII absorption threshold allows the computing of the contribution of anomal atoms in the total diffraction signal. It is then possible to distinguish the two different structure factor modulus involved in the diffraction: FN corresponding to normal atoms (Silicon) and FA corresponding to anomal atoms (Gold), given within a scaling factor. The total structure factor modulus FT (normal + anomal) is also displayed for comparison with GIXD, the latter being an image of the first. The positions of the peaks of the FT signal are indeed consistent with the fitted peaks of the GIXD experiments (see ref 1): one peak is found at the same H value (H≈2.9988) for sample B, and two peaks are visible for sample C close the ones found in GIXD near H≈2.9982 and H≈2.9995. For as grown wires of group A it is clear on figure (a) that gold is present in the crystalline matrix of the wires and contributes to the diffraction signal as revealed by the great amplitude of the anomal part close to the nanowire peak. A closer look at the MAD signals reveals that the maximum of the anomal signal is located at a smaller H (larger lattice parameter) than the normal signal corresponding to the nanowires. We conclude that the regions where gold is present are more dilated than the regions where it is absent, which is consistent with previously reported results. Since the analysis of GIXD (See ref 1) led us to assume that the dilatation strain is increasing from the center of the wire up to its surface, it can be deduced that gold is mainly located on the sides of the nanowires. After standard chemical gold removal by I-KI, the MAD analysis of group B (Fig. b) also reveals an anomal signal in the nanowires. Its intensity is still important and has the same features than the one with as-grown wires. A strong contribution of gold appears close to the silicon nanowire peak, at a lower H, but a secondary peak is also present in the anomal signal closer to the silicon one at H≈2.9988. This can be interpretated as the signature of the segregation of the contamination between the center and the surface of the nanowires. This result implies that even if gold has been roughly removed from the external surface of the wires by chemical etching, there is still some contamination as diluted atoms in the silicon matrix close to the surface of the nanowire, but also in the center of the structure at a lower level. In conclusion I-KI wet etching is efficient to remove superficial gold on CVD-VLS grown silicon nanowires but is ineffective to thoroughly remove all traces of catalyst from the entire structure which therefore remains contaminated.



To further clean the wires of group C from gold, a layer of 18 nm of silicon was etched from their surface by successive thermal oxidation and HF etching. Figure (c) confirms this analysis since the two different diffraction peaks C and S (see Ref 1) are found again in the MAD signal. We easily distinguish the two separate peaks in the normal signal, and we clearly see an anomal contribution for each of them, attesting that there is still some gold remaining in the whole nanowires. Nevertheless the anomal signal is weak, hardly out of the noise, meaning that the thermal oxydation - HF etching cycle managed to remove a bit more of the remaining gold after chemical etching. In order to compare the contribution of gold in both center and periphery of the nanowires, the ratio r = FA=FN between the anomal (Au) and normal (Si) signal is calculated at the corresponding H values.

Figure: MAD analysis along the [100] direction (plots) and proposed corresponding physical state of silicon nanowires (illustration sketches). (a) As grown nanowires of group A. (b) Nanowires after chemical gold etching of group B. The FT peak related to GIXD is located by the dashed line. (c) Thermally treated nanowires of group C, peaks C and S of FT are emphasized by the vertical dashed lines.

To conclude we showed that standard wet chemical etching of the gold catalyst of CVD-VLS grown silicon nanowires is not efficient enough to clean all traces of gold. The nanowires remain strained and contaminated by catalyst residues. Neither the sequence of thermal oxidation followed by HF deoxidation is not efficient enough to totally remove the contamination. Gold is still present in the wires probably because of its strong diffusion during the thermal oxidation step. These chemical and physical treatments create a "core-shell like" structure in the nanowires, featuring a center which is less strained and contaminated than the periphery. One interesting follow up investigation will be to physically etch the surface of the nanowires in isotropic mode and at low temperature to prevent any gold diffusion during the etching.

Reference:

1 L. Dupré, D. Buttard, C. Leclere, H. Renevier, P. Gentile, “Gold removal efficiency by thermal oxidation cycle in silicon nanowires grown by chemical vapour deposition : Multiwavelength Anomalous Diffraction investigations”*Chemistry of Materials*, **24** 4511-4516 (2012).