

In Situ TEM Studies of Metastable Hexagonal Close-packed Au Nanocatalysts at the Tips of Ge Nanowires

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Nanoscale materials such as nanowires offer novel pathways for metastable phase formation, as well as the potential to observe these phases forming in real time during in situ TEM experiments. Examples of metastable phase formation as a result of nanowire growth include the observation of hexagonal close-packed Ag nanowires [1-4], and the formation of a hexagonal close-packed (hcp) Au nanocatalyst at the tips of Ge nanowires [5]. The unusual observation of hcp Au, which was not reproduced by in situ TEM heating and cooling of nanowires in a standard furnace holder, was attributed to Ge supersaturation of the liquid eutectic particle during nanowire growth, allowing transient access to the metastable hcp beta alloy phase during cool-down [5]. More recently Gamalski et al. have observed the formation of Au-Ge metastable phases during in situ isothermal growth of nanowires far below the eutectic temperature [6].

The morphology of nanowires provides a rather unique structure for in situ heating and cooling studies, with a small, defined volume of catalyst remaining at the end of the nanowire, and an isolated interface for characterization of melting, crystallization and phase formation. To the extent that these behaviors are reversible, the same sample can be cycled repeatedly to explore specific parameters such as quenching rates. Here we report on the TEM observation of the metastable hexagonal close-packed structure occurring in a Au nanoparticle with a Ge content much less than that reported for the metastable beta phase, which formed as a result of rapid quenching of nanowires in a MEMS-based heating holder (Protochips AduroTM). Fig. 1 shows a catalyst particle that has been heated to form the eutectic liquid and then rapidly quenched. Note that this Au particle contains on the order of 6-10 at% Ge, as measured by EDS, i.e. far less than the 16 to 25 at% Ge reported for the beta phase that occurs as a result of splat cooling experiments reported in the literature [7].

The amount of Ge that is observed to remain in the hcp Au structure during TEM quenching appears to be higher than that previously reported following nanowire growth, which was on the order of 3 at% or less. Furthermore it appears that Ge diffuses into and out of the hcp phase as a function of temperature suggesting that the amount of Ge in the structure can be controlled by temperature. Fig. 2 shows such a melted, then quenched nanocatalyst that has the hcp structure. During re-heating the particle interface moves toward the tip and Ge deposits on the end of the nanowire. As the nanoparticle is heated further the process reverses, and the interface moves in the direction of the nanowire indicating that, approaching the melting temperature, Ge diffuses back into the hcp structure. This apparent easy diffusion of Ge into and out of the hcp structure as a function of temperature may explain both the wide range of compositions reported for splat cooling experiments, which involve much larger volumes of material than that of nanowires, and the variations in the residual Ge in Au that we observe for nanowire growth (almost pure Au) compared to that for rapid quenching in the Aduro holder.

We are also investigating methods to quantify the amount of hcp phase formed under different synthesis conditions such as the effect of having germane gas present during nanowire cool-down at the end of growth. Fig. 3 shows an X-ray diffraction pattern where we have used the relative intensities of the fcc

111 peak and the hcp 101 peak to estimate the amount of hcp phase formed. The results indicate that a higher activity of Ge in the growth chamber does indeed increase the amount of hcp formed following nanowire growth. We are also investigating the use of electron diffraction to determine the amount of the hcp phase in the sample. Fig. 3 also shows preliminary results in obtaining selected area diffraction (SAD) of nanocatalysts that have been chemically removed from the nanowires.

References:

- [1] X. Liu, J. Luo and J. Zhu, *Nano Lett.* **6** (2006), 408.
- [2] C. Liang, *et al*, *Jpn. J. Appl. Phys.* **45** (2006), 6046.
- [3] A. Singh and A. Ghosh, *J. Phys. Chem. C* **112** (2008), 3460.
- [4] Y. Zhou, *Nanotechnology* **19** (2008), 285711.
- [5] A.F. Marshall, *et al*, *Nano Lett.* **10** (2010), 3302.
- [6] A.D. Gamalski, *et al*, *Phys. Rev. Lett.* **108** (2012) 255702.
- [7] H. Okamoto and T.B. Massalski, *Bull. Alloy Phase Diagrams* **5** (1984), 604.
- [8] The authors acknowledge National Science Foundation grant DMR-1206511 for financial support. Use of the facilities of the Stanford Nanocharacterization Laboratory is appreciated.

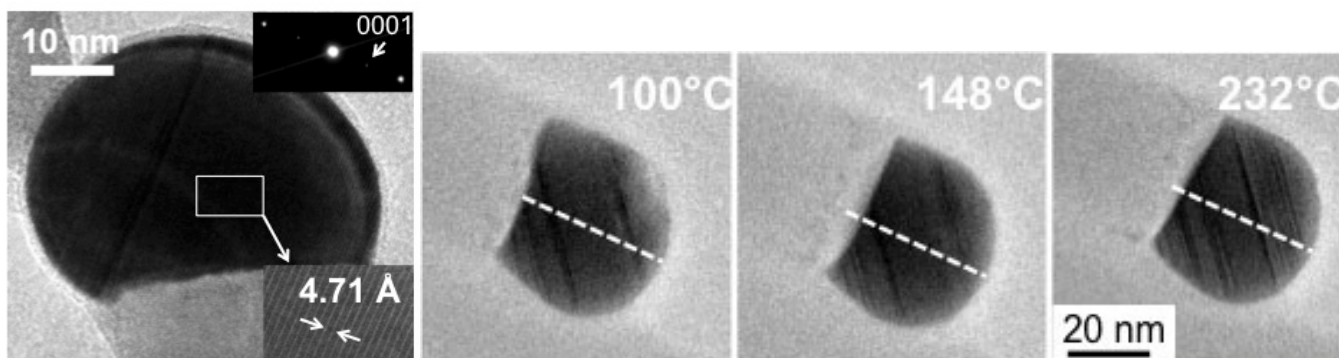
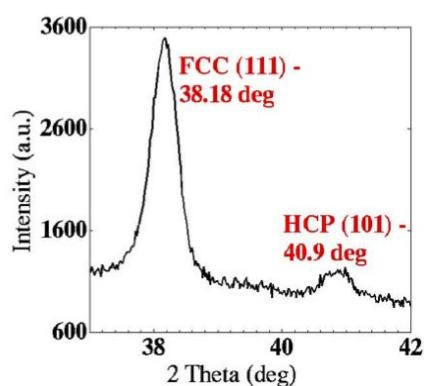


Figure 1. The hcp structure of a Au catalyst on a Ge nanowire that has been melted and quenched in the TEM. The Ge content is on the order of 6-10% as measured by EDS.

Figure 2. A similarly quenched hcp Au particle observed during re-heating. The interface moves to the right approximately 3-4 nm, and then back to the left approximately 1-2 nm as Ge first deposits on the NW and then moves back into the hcp structure. The dotted line is the same length in all three images.



Germane Partial Pressure (torr)	Cooling Condition	% HCP
0.75	No germane	13
0.75	Germane present	38
1.2	Germane present	43

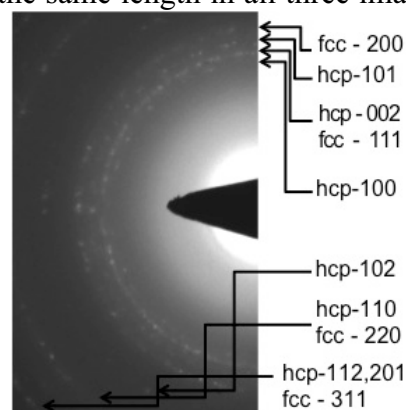


Figure 3. XRD analysis of Au nanocatalysts in as-grown Ge nanowires indicates that the amount of hcp increases when germane is present during the cool-down; SAD of Au nanocatalysts that have been chemically removed from the nanowires.