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Molecular Beam Epitaxy of Germanium in the Atomic-Resolution Transmission Electron Microscope.

Éric Ngo¹, Federico Panciera², Jean-Christophe Harmand², Weixi Wang¹, Martin Foldyna¹, Pere Roca i Cabarrocas¹, Laurent Travers², Ileana Florea¹ and Jean-Luc Maurice¹.

¹ LPICM, CNRS, École polytechnique, 91128 Palaiseau, France,

² C2N, CNRS, Université Paris-Sud-11, Université Paris-Saclay, 91120 Palaiseau, France.

Molecular beam epitaxy (MBE) is an atomically precise method for making monocrystalline thin films or nano-objects. Aberration-corrected transmission electron microscopy allows one to observe crystalline solids at the atomic scale. Combining the two techniques has been an old dream among materials scientists as it allows one to watch the nanostructures growing atom by atom. However, and despite the ripeness of those two methods, this dream has only become true recently [1,2] with the NanoMAX transmission electron microscope (TEM) used in the present work; a modified Thermo Fisher Titan environmental TEM that is fitted with molecular beam effusion sources. In the present communication, the potential of this combination is illustrated by the observation of step-by-step growth at the surface of germanium nanowires (NWs) as a function of temperature, notably at low temperatures, where *in situ* chemical vapour deposition (CVD, see e.g. [3]) would probably not have worked.

The growth proceeds through the vapour-liquid-solid (VLS) mechanism [4], using Au as catalyst. The heating sample holder is a modified Protochips Fusion holder. Firstly, upon increasing the Ge content of Au nanoparticles, we observe at 400°C the solid to liquid transition associated with eutectic formation. Measuring the increase of droplet size as a function of time (Fig. 1), we deduce (i) the Ge flux (~ 5 at. $\text{nm}^{-2}\text{s}^{-1}$) and (ii), the Ge content when particles become fully liquid. We find that this happens above ~ 27 Ge at. %, which is consistent with the bulk phase diagram where, at 400°C, the liquidus curve is met at $\sim 26.2\%$ [5].

With MBE, the NW growth may be essentially axial or radial depending on whether the surface diffusion of Ge adatoms is respectively high or low, feeding the growing crystal respectively through the catalyst or through the walls directly. Decreasing deposition temperature should then promote sidewall growth by decreasing surface diffusion. Going from 450°C to 200°C, we observe indeed the development of sidewalls: at medium temperature ($\sim 350^\circ\text{C}$), NWs acquire a pyramidal shape (Fig. 2a). Quite remarkably, it allows us to observe standard epitaxy viewed in cross-section on the NW walls (Fig. 2b).

A good crystalline stacking is ensured on such a side-wall when an atom finds its equilibrium position before it is stuck in place by the incoming flux. Here, when lowering the deposition temperature at constant flux, stacking faults occur at 200°C. Upon further decrease of the temperature, the surface mobility becomes so low that no crystalline stacking is allowed: at room temperature, the deposited material is amorphous (Fig. 2b).

The presentation will show the movies from which the figures have been extracted. The present study is part of a project, the aim of which is to understand how, in certain conditions of growth, the diamond stacking of atoms in Ge and Si NWs may adopt a hexagonal polytype [6] that would have, in turn, specific and interesting opto-electronic properties [7] [8].

- [1] J-C Harmand, G Patriarche *et al*, (2017), Nanowire week, Lund, Sweden.
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 [7] M Amato, T Kaewmaraya *et al*, *Nano Lett.*, **16** (2016), p. 5694.
 [8] This work is partly supported by the French national research agency ANR, through the TEMPOS Equipex (ANR-10-EQPX-50) (NanoMAX) and the HexaNW project (ANR-17-CE09-0011).

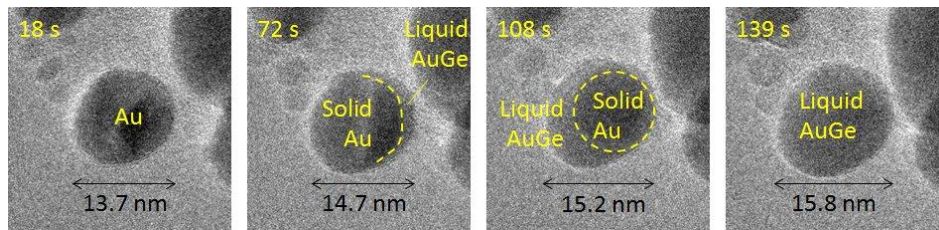


Figure 1. TEM images of an AuGe particle during bombardment by Ge atoms at 400°C. The material becomes liquid as the Ge concentration reaches the eutectic one. The size measurement allows one to infer the number of Ge atoms present in the droplet and deduce the Ge flux.

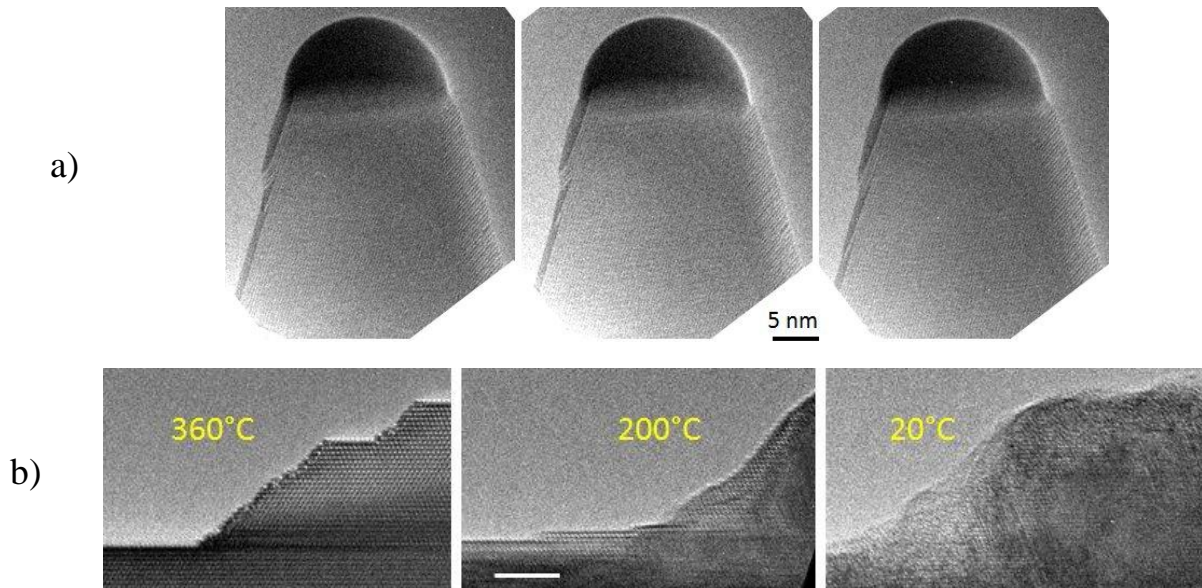


Figure 2. Advancing atomic steps on {111} sidewalls. (a) Three successive frames of a typical pyramidal Ge NW, viewed about 10° off the [110] zone axis at 350°C. See the movement of the individual atomic step on the left {111} wall. The time between two frames is 0.25s. (b) Effect of temperature: {111} sidewall similar to that of (a), viewed in the [110] zone axis, and pictured at the three temperatures indicated. Note surface smoothing and introduction of crystalline defects at 200°C, and of amorphous structure at 20°C. Scale bar 5 nm.