

## Si and Ge nanowire growth mechanisms observed using *in situ* microscopy

S. Kodambaka, J. B. Hannon, R. M. Tromp, M. C. Reuter, J. Tersoff and F. M. Ross

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA

Nanowires are narrow, long crystals that are formed when a catalyst particle is used to increase the growth rate at one location on a crystal surface. This catalytic growth process has several features that make it very promising for applications in nanotechnology. It can be used to form small structures without the limitations imposed by lithography; the structures can be grown at controlled locations on a wafer, and furthermore, the process allows the integration of different materials, such as wires made of compound semiconductors grown on a silicon substrate. Nanowires have already been demonstrated as functional components in transistors, optoelectronic devices, logic circuits and sensors. Single crystal and heterostructure wires also have great promise in devices such as wrap-gate (vertical) transistors and other three dimensional structures.

A major challenge in the implementation of nanowire-based technology is the development of parallel, scalable, and reproducible fabrication techniques. Current approaches based on growth, harvesting, and placement of nanowires are suitable for single device demonstration but not for manufacturing. In order to develop these techniques, it is important to acquire a detailed understanding of nanowire growth. This will ensure that wire diameter, composition, direction and even branching can be controlled at every location across the wafer where a nanowire is required.

In this presentation, we will describe the contributions of *in situ* microscopy to understanding the growth kinetics of nanowires in the Si/Au and Ge/Au systems. We have examined nanowire growth *in situ* in two microscopes, a TEM and a LEEM, both of which have an ultra high vacuum base pressure. Growth experiments were carried out by preparing an Au-covered Si(111) surface *in situ*, and then exposing to disilane or digermane gas at a growth temperature between 350 and 650°C. On heating, the initially continuous Au film forms a Si-Au eutectic and agglomerates into droplets of different sizes. Dissociation of the gas supplies additional Si (or Ge) to the droplets. This diffuses through the droplets and precipitates at the droplet-substrate interface, resulting in the formation of a column beneath each droplet with a diameter controlled by the droplet volume [1]. This process can be seen directly, in real time, in the TEM (Fig. 1a), while the evolution of the surface structure between the wires, and the droplet sizes during growth, can be seen in the LEEM; wires grown in the LEEM can be imaged post-growth by SEM (Fig. 1b).

By observing nanowires as they grow, we can examine their structure under growth conditions, avoiding artifacts such as surface oxidation caused by removal from the growth chamber and exposure to the atmosphere. Such observations show that Si wire sidewalls have an interesting structure. Instead of being flat <211> surfaces, they show a periodic sawtooth faceting [2]. This can be explained by a balance between droplet surface tension, sidewall energy, and interface energy, and may affect electronic properties such as carrier scattering.

*In situ* microscopy also enables us to examine the growth kinetics of individual wires quantitatively, and to determine directly the effects of changes in parameters such as gas species, pressure, and temperature. By comparing the growth rate of wires of different diameter, we find that the rate

limiting step during Si nanowire growth is the irreversible dissociative adsorption of disilane on the droplet surface [3]. And by examining the evolution of individual nanowires, we find, surprisingly, that the catalyst droplets change during wire growth [4]. Most droplets shrink during growth and may even disappear (Fig. 1a), so that the wires have a conical shape and a limited length, since they can not grow once the droplet has vanished. Some droplets increase in size, however, leading to wires that widen as they grow (Fig. 1b). The reason for these size changes is twofold. Firstly, a surface coverage of Au is seen by LEEM, and as the wires lengthen, catalyst is used up to cover the wire surface and all droplets shrink. Secondly, Ostwald ripening of the droplets takes place, mediated by Au diffusion along the wires and across the surface between them, causing some droplets to grow while most shrink. A changing wire diameter is a disadvantage as it means that the electronic properties of a wire are likely to vary with position along the wire. Fortunately, the introduction of low background pressures of oxygen during growth hinders Au surface diffusion, allowing parallel sided wires to be grown [5]. Ge nanowires have also been grown *in situ*, and we find that in this case surface diffusion of Ge adatoms plays a role in wire surface structure and growth kinetics.

These results show that *in situ* microscopy techniques can be helpful in explaining some of the phenomena controlling wire growth. Sidewall faceting, redistribution of catalyst onto the wire surfaces, and changes in wire diameter may all affect the electronic properties and influence the growth of simple wires, as well as more complex branched or core-shell structures. The understanding obtained from *in situ* experiments may allow us to design growth regimes that will form optimal structures. As nanowires are used in an increasing range of novel devices, precise control at the nanoscale will become even more important and microscopic techniques will hopefully have a significant role to play in developing wire-based nanoscience and nanotechnology.

## References

- [1] R.S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* 4 (1964), 89.
- [2] F.M. Ross, J. Tersoff, M.C. Reuter, *Phys. Rev. Lett.* 95 (2005) 146104.
- [3] S. Kodambaka, J. Tersoff, M.C. Reuter, F.M. Ross, *Phys. Rev. Lett.* in press (2006).
- [4] J.B. Hannon, S. Kodambaka, F.M. Ross, R.M. Tromp, *Nature*, in press (2006).
- [5] S. Kodambaka, J.B. Hannon, R.M. Tromp, F.M. Ross, submitted (2006).
- [6] We acknowledge the support of DARPA-SPAWAR under contract N66001-05-C-6030.

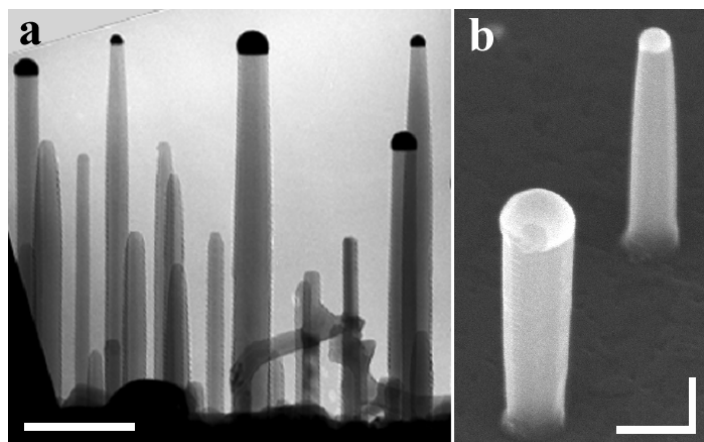


FIG. 1. (a) Si nanowires grown using Au-Si catalyst, imaged in bright field. The wires were grown using chemical vapour deposition of Si from disilane at 645 °C and  $1 \times 10^{-6}$  Torr for 240 mins. The beam is almost parallel to [1-10]; each droplet forms a wire growing in the (111) direction with  $\langle 211 \rangle$  sidewalls. Au-Si eutectic droplets (dark) are visible on some wires, but many wires show no droplets due to coarsening. Scale bar 500nm. (b) Two nanowires, one widening and one narrowing, grown at 600 °C and  $1 \times 10^{-6}$  Torr disilane. SEM image at 42° angle of incidence; scale bars 200nm.