Growth of epitaxial InAs nanowires in a simple closed system

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The epitaxial growth of InAs nanowires on an InAs(111) substrate in a sealed quartz tube is described. The method is quite simple and fast, and uses only a bare InAs substrate and a gold colloid coated InAs(111) substrate. High quality InAs nanowires can be produced by this technique, with the nanowire diameter controllable by the variation of growth temperature. The composition of the seed particle at the tip of the nanowire indicates that the nanowires grew via the vapor-liquid-solid growth mechanism but with Au–In as the liquid alloy. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1999846]

There has been a rapid advance in recent years in the methods available for fabricating various nanowires. For InAs in particular, it is an attractive semiconductor for application in high performance electronics due to its high electronic mobility. Several methods of InAs nanowires and whisker growth have been reported, including metalorganic vapor phase epitaxy (MOVPE)[1] and chemical beam epitaxy (CBE),[2] in which the wires were grown epitaxially with the substrate. The growth of loose InAs wires has also been reported by laser-assisted catalytic growth (LCG)[3] and a vapor method using In metal and a GaAs substrate, with a growth time of 36 h.[4] In this letter, we report on a very simple and inexpensive method to grow InAs nanowires epitaxially over a large area on an InAs(111) wafer. This growth technique results in high quality, stoichiometric InAs wires, and there is no need to prefabricate complex target materials, use toxic gases or solid As sources, nor subject the sample to lengthy growth times. In our growth method, we use only a bare InAs substrate and a gold colloid-coated InAs(111)substrate inside a sealed quartz tube. Our method is strictly based on the utilization of the temperature gradient that exists inside the furnace, where the source substrate evaporating at the hotter temperature region provides vapor for the nanowire growth in the lower temperature region.

The InAs nanowires were grown inside a sealed quartz tube in an open tube furnace. The native oxide on the InAs substrates was removed by chemical etching in HCl:H_2O (1:10). Gold colloid (20 nm, from Ted Pella, Inc.) drops were placed on the InAs(111) substrate, which was immediately loaded, along with a bare InAs substrate, inside a quartz tube (10 mm in diameter), which was evacuated to 70 mTorr and sealed with a torch. The center of the furnace was raised to 875 °C, and the quartz tube was inserted into the furnace. Inside the quartz tube, the bare InAs substrate was positioned at the hottest point in the furnace, while the gold-colloid coated InAs(111) substrate was placed toward the cooler end of the furnace, where the temperature was 540 °C. The tem-

perature was measured in a control experiment in which a thermocouple was inserted into the quartz tube to the correct position, with an accuracy of 5 °C. The quartz tube was then annealed for a specific time period. After the desired annealing time, the quartz tube was immediately removed from the hot furnace and allowed to cool, either by cooling in air (about 5 min) or very rapid cooling in a water bath (several seconds). The grown nanowires were analyzed using a LEO SUPRA 55 scanning electron microscope (SEM), JEOL 2010F 200 KV high resolution transmission electron microscope (HRTEM) and x-ray energy dispersive spectroscopy (EDS) attached to the HRTEM.

An image of the nanowires grown inside the sealed quartz tube is shown below. Figure 1 is a SEM image of the nanowires which were grown for 20 min. As can be seen, the nanowires grow predominantly perpendicular to the InAs(111) substrate, with diameters of the nanowires varying from 20 to 70 nm, with an average height of about 1 μm. Figure 2 shows a SEM image of the nanowires grown at the same temperature, but for longer annealing time, in this case, 1 h and 30 min. The diameter of the nanowires was similar to those in Fig. 1 (20 min anneal), but their height increased to about 5 μm (on average). We found, in general, that the length of the nanowires was controlled by the length of the
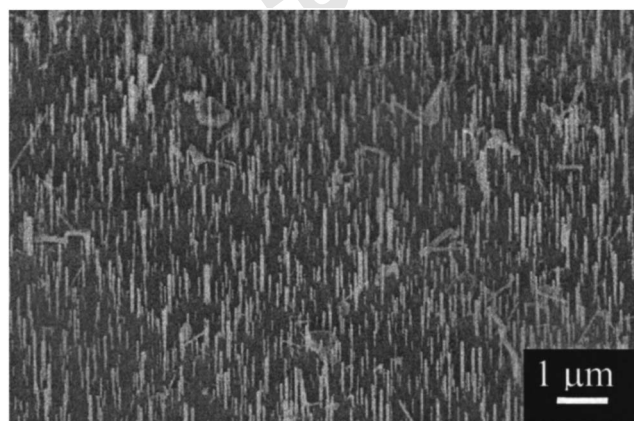

FIG. 1. Growth of InAs nanowires at 540 °C for 20 min.

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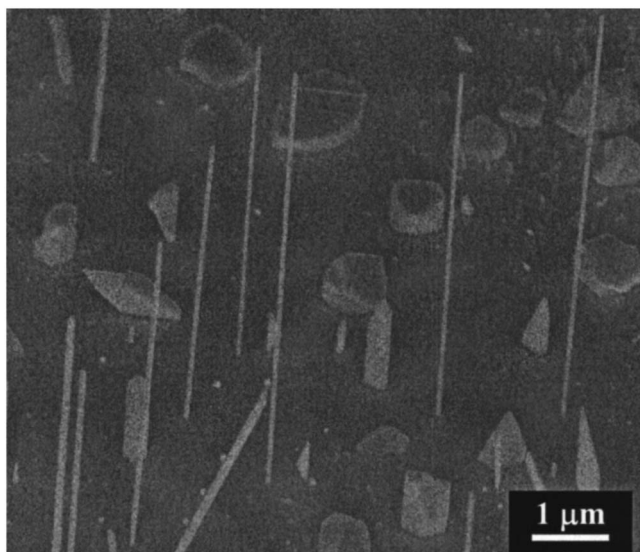
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FIG. 2. Growth of InAs nanowires at 540 °C for 1 h, 30 min.

annealing time at a set temperature, while the width of the average nanowire was found to increase with higher annealing temperatures. Due to the rapid cooling process, it is not expected that nanowire growth would occur upon cooldown.

The HRTEM image of the nanowire, revealing the lattice fringes, is shown in Fig. 3, with a scale bar of 5 nm. The insets show the corresponding selective area electron diffraction (SAED) pattern and the nanowire tip. The electron diffraction pattern shown was imaged down the [011] zone axis. From these results, the measured lattice spacing along the (111) direction is 0.344 nm, corresponding to the lattice spacing of bulk InAs. In Fig. 4(a), the result of the HRTEM EDS performed on the nanowire is shown, with the As and In peaks marked. Quantitative analysis indicated a 52.1 and 47.9 at. % of In and As, respectively. The Cu peaks are from the TEM grid.

The HRTEM EDS was also performed on the seed particle at the tip of the nanowire, as shown in Fig. 4(b). It was
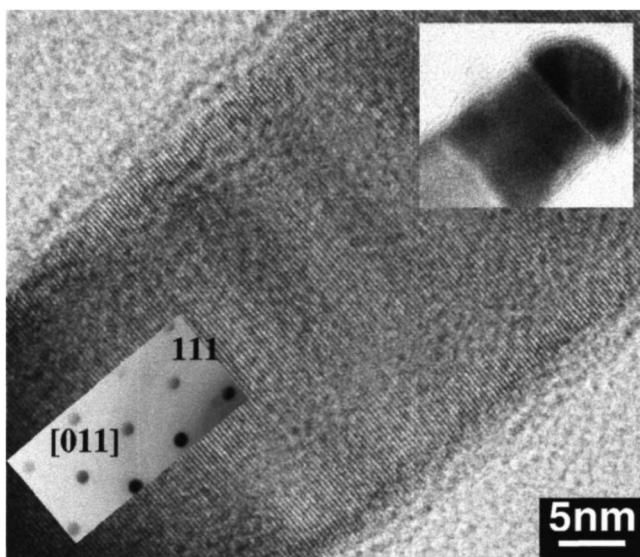

FIG. 3. HRTEM images of an InAs nanowire, with insets showing the corresponding SAED pattern and the seed particle at the tip of the nanowire.
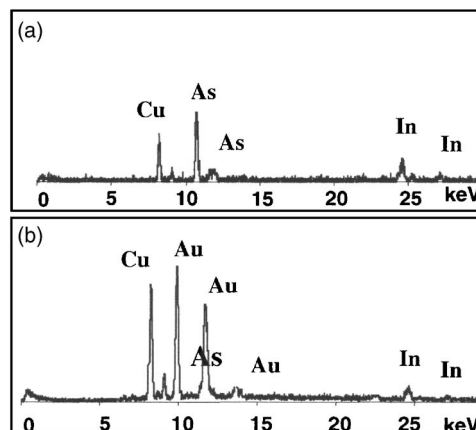

FIG. 4. HRTEM EDS on the (a) nanowire, and (b) seed particle. The Cu peaks are due to the copper TEM grid.

found to consist primarily of In and Au (about 32 and 60 at. %, respectively), with a small amount of As. The small amount or complete absence of As in the seed particle have been documented previously in other III-As nanowire studies (both in LCG[3] and CBE[5] grown GaAs nanowires), using Au as the metal catalyst. In the LCG case, the laser target was prefabricated specifically based on the pseudo-binary phase relationship of Au forming a liquid alloy with GaAs in accordance with the vapor-liquid-solid (VLS) growth mechanism.[6] The authors then attributed the presence of Ga in the Au to the possible formation of an amorphous Ga(O) layer coating. In the CBE case, the seed particle was also found to contain an alloy of Ga and Au, but the authors described their growth in terms of the VSS growth mechanism. In our results, the detected concentration of In corresponds to a liquid phase according to the Au–In binary phase diagram at 540 °C. Consequently, this result suggests that our InAs nanowires grew according to the VLS mechanism, but with a Au–In as the liquid alloy, and not Au–InAs.

When Au interacts with group III-V, the following reaction occurs:[7,8]

$$Au + III\text{-}V \rightarrow Au\text{-}III + V(\text{elemental solid or gas})$$
$$+ Au\text{-}V.$$
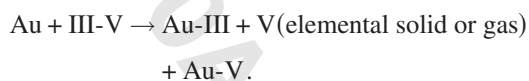
For the Au interaction with InAs, the products are AuIn, and As. Au–As is not considered since no compound can form and, in fact, it has been shown previously that As simply diffuses out of the Au.[9,10] In our experiments, in the early stages of annealing, the quartz tube is under vacuum, and the semiconductor substrate undergoes a decomposition process, releasing volatile As with the rapid rise in temperature. Depending on the temperature and the In and Au content, the AuIn catalyst on the surface of the substrate could consist of several possible solid intermetallic phases, or a liquid phase. Since at 540 °C (the temperature of our growth), the solubility[9] of In in Au is only about 11.5 at. %, the greater amount of In (>at. % 30) which we found in the tip suggests that the Au and In form a liquid at this temperature. Since our system is closed, equilibrium in the In and As vapors is established inside the quartz tube with annealing, and nanowire growth via the VLS is then possible, due to the presence of the liquid Au–In catalyst.

Recently, Dick et al.[11] suggested that the growth of InAs

nanowires by MOVPE involves a solid Au–In alloy particle, contrary to the VLS mechanism. However, there are significant differences in the growth experiments, which precludes us from making a direct comparison at this point. These differences include the very different initial base pressures (different oxygen content) and a very different growth process (decomposition of precursors versus simple evaporation and atom migration). Furthermore, the use of hydrogen gas by Dick *et al.* could also significantly affect the growth, since it has been reported[12] that hydrogen plays a major role in nanowire growth by enhancing atomic mobility.

In conclusion, we have described a very simple method to grow InAs nanowires by using a sealed quartz tube at a temperature of 540 °C. Despite the simplicity, the new growth method yields single crystalline, stoichiometric InAs nanowires, which grow epitaxially on an InAs(111) substrate. The quantitative analysis performed on the seed particle suggests that the growth of the nanowires proceeds via the VLS mechanism with Au–In acting as the liquid alloy catalyst.

[1] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, J. Appl. Phys. **77**, 447 (1995).

[2] L. E. Jensen, M. T. Bjork, S. Jeppesen, A. I. Persson, B. J. Ohlsson, and L. Samuelson, Nano Lett. **4**, 1961 (2004).

[3] X. Duan and C. M. Lieber, Adv. Mater. (Weinheim, Ger.) **12**, 4, 298(2000).

[4] M. He, M. M. E. Fahmi, S. N. Mohammad, R. N. Jacobs, L. Salamanca-Riba, F. Felt, M. Jah, A. Sharma, and D. Lakins, Appl. Phys. Lett. **82**, 21 (2003).

[5] A. I. Persson, M. W. Larsson, S. Stenstrom, B. J. Ohlsson, L. Samuelson, and L. R. Wallenberg, Nat. Mater. **3**, 677 (2204).

[6] E. I. Givargizov, Krist. Tech. **10**, 473 (1975).

[7] C. T. Tsai and R. S. Williams, J. Mater. Res. **1**, 352 (1986).

[8] J. H. Pugh and R. S. Williams, J. Mater. Res. **1**, 343 (1986).

[9] M. Hansen, *Constitution of Binary Alloys* (McGraw–Hill, New York, 1958), p. 211.

[10] Y. Yamamoto and K. G. Stephens, Thin Solid Films **60**, 123 (1979).

[11] K. A. Dick, K. Deppert, T. Martensson, B. Mandl, L. Samuelson, and W. Seifert, Nano Lett. **5**, 761 (2005).

[12] S. M. Prokes and S. Arnold, Appl. Phys. Lett. **86**, 193105 (2005).