Study of the initial nucleation and growth of catalyst-free InAs and Ge nanowires

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The authors have examined the nucleation conditions in the growth of catalyst-free InAs and Ge nanowires (NWs) on porous Si, as well as the growth of InAs NWs on a SiO_2 substrate using 10 nm sized In nanoparticles. The NW growths were performed in a closed system. The results suggest that all the NWs grew from a solid nucleation state. For the growth using In nanoparticles, the results suggest that the growth mechanism is very different from the vapor-liquid-solid, in that the nanowire growth only begins after the nucleation particle solidifies. © *2007 American Institute of Physics.*
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Various nanowires (NWs) have been grown over the years via growth mechanisms such as vapor-liquid-solid (VLS),[1] solution-liquid-solid,[2] and oxide assisted (OA),[3] using metal catalyst and presumably metastable oxides. There also have been reports of catalyst-free NW growths, such as III-V and II-VI,[4] ZnO (Ref. 5) on quartz tube, GaN (Ref. 6) on Si(111), and ZnO (Ref. 7) and GaAs (Ref. 8) on porous Si. Despite the fact that no catalyst was used in these reported growths, the growth mechanism, specifically the nucleation conditions, is very unclear. The nature of the nucleation condition is complicated by the fact that one of the nanowire components has a very low melting point (Zn: 419 °C, Ga: 29.7 °C) compared to the higher growth temperature, which can potentially serve as a liquid nucleating center. Previously, a growth mechanism similar to the VLS has been proposed to explain the growth of catalyst-free ZnO NWs, namely, the self-catalyzed VLS growth model,[5,9] where the NWs are supposedly grown from a liquid droplet of Zn. Clearly, much work is still needed to clarify the nature of the nanowire nucleation conditions.

In this letter, we examine these issues by studying the NW growth of InAs as well as Ge (which does not form any eutectic with Si (Ref. 10) and which has a high melting temperature) in porous Si, as well as InAs NWs growth using In nanoparticles (melting point of 156.6 °C). With these results, we demonstrate not only that all the NWs are grown from a solid nucleating center but also the growth of catalyst-free Ge NWs that has not been reported before. Previously, Ge NWs have been grown primarily by using a Au catalyst via the VLS growth mechanism.[11–13] More interestingly, from the growth of the InAs NWs using the In nanoparticles, we also show a NW growth mechanism which appears to be very different from any known NW growth mechanism reported to date.

The NWs were grown in a closed, quartz tube system (the details of which are reported in our previous papers).[14,15] For the growth using the porous Si, InAs (Ge) source substrates were placed inside the quartz tube with the fresh porous Si, evacuated to 30 mTorr, and torch sealed. The porous Si was produced by etching 1 Ω cm *p*-type Si(100) samples at 30 mA/cm² for 30 min in 25% HF-ethanol solution. In general, the outer etched regions of the porous silicon exhibited higher porosity and higher stress than the center regions, due to the specific geometry of the masked Si region which led to nonuniform etching conditions. For the Ge NWs synthesis, the higher porosity outer regions were used. To remove the native oxide, the Ge substrate was treated with buffered HCl and de-ionized water. For the Ge NW synthesis, the furnace temperature was set at 980 °C and the Ge source substrate was placed at the highest temperature. The Ge and InAs NWs were then grown for 30 min at 400–500 and 580 °C, respectively, with no catalyst. For the growth involving the In nanoparticles, 10 nm sized In nanoparticles (Meliorum Tech) were solution dispersed onto a SiO_2 substrate and placed inside a quartz tube (along with the InAs source substrate), evacuated to 30 mTorr, and torch sealed. A LEO scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) attached to LEO SEM were used to examine the NWs.

The SEM images of the various nanostructures grown on the porous Si with varying degrees of porosity from lower (center) to the higher (edge) porosity are shown in Figs. 1(a)–1(e), respectively. In the lower porosity regions, large irregularly shaped nanostructures (sometimes with ~50 nm-sized NWs) and nanobelts were found, as shown in Figs. 1(a) and 1(b), respectively. With an increase in the porosity, NWs were found to grow, as shown in Figs. 1(c)–1(e), all with similar diameters, generally <20 nm.

In Fig. 2, the angled-SEM images of the Ge NWs that were grown on porous Si are shown. The insert is the close-up view of the Ge NWs. Interestingly, all the NWs were also <20 nm in diameter. The close-up view shows some of the nanowires growing upward from the substrate. The EDS confirmed the NWs to be Ge.

In Fig. 3, the SEM image of the InAs NWS grown on a SiO_2 substrate with 10 nm In nanoparticles is shown. The scale bars are 300 nm for Fig. 3(a) and 100 nm for Figs. 3(b)–3(d). The NWs were predominantly found with dropletlike nanostructures attached along the length [primarily on one side, as shown in Fig. 3(a)], but a few NWs were also found with smooth surfaces. The nucleation region at the bottom of the NWs, shown in Figs. 3(b)–3(d), exhibits liquid migration prior to the growth of the NWs. Interest-
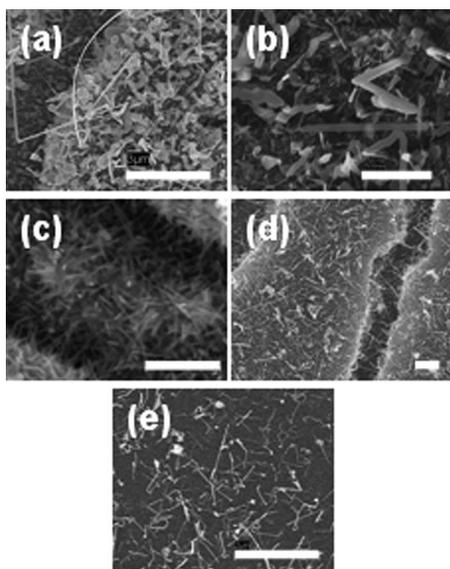
FIG. 1. Growth of nanostructures, nanobelts, and NWs on a porous Si with varying degrees of porosity from (a) lowest (center) to the (e) highest (edge) porosity. Scale bars are (a) 3 μm, (b) 500 nm, (c) 500 nm, (d) 1 μm, and (e) 2 μm.

ingly, despite the apparent size of the initial liquid region, the NWs were all <15 nm in diameter.

With the above results, let us now examine the nucleation conditions closely, beginning with the growth using the In nanoparticles. Due to the low melting point, In nanoparticles should be in a liquid state at the NW growth temperature of 580 °C. The liquidlike migration on the substrate surface suggests a vapor impingement stage, in which In and As vapors keep arriving and adsorbing onto this droplet, until the droplet solidifies. This in turn suggests that the NW actually grows only when a solid nucleation state is established; otherwise, one would have expected the nanowires to grow immediately, without the liquid migration first. Analogous to the VLS growth mechanism, this growth also involves all three states: vapor, liquid, and solid, but unlike VLS, there are three significant differences. This growth mode does not require a supersaturation, the growth front is solid (i.e., liquid is no longer part of the growth process once the NW begins to grow), and since In is one of the components of the growing NW (unlike Au metal catalyst which is a foreign impurity), there is no "alloy" tip at the end of the NW. Thus instead of VLS, this growth mechanism is correctly depicted as vapor-liquid-solid-solid. It should be mentioned that unlike the catalyst-free NW growth mechanism,[4]
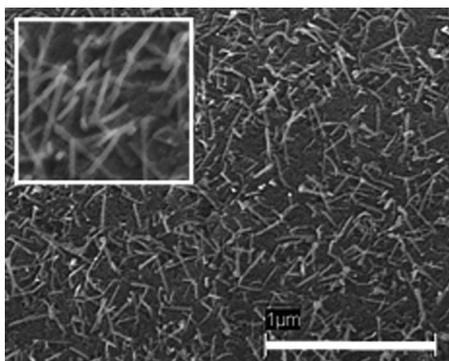

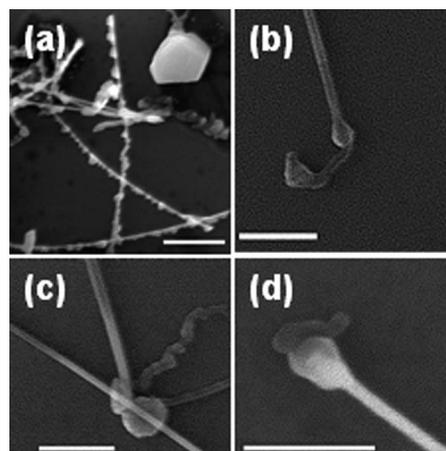FIG. 2. Growth of Ge NWs on a porous Si substrate.

FIG. 3. InAs NWs grown on a SiO$_2$ substrate using 10 nm In nanoparticles, where (a) is the typical NW growth and (b)–(d) show the liquid migration prior to the NW growth. Scale bars are 300 nm for (a) and 100 nm for (b)–(d).

this growth mechanism requires no supersaturation in order for the NW growth to begin. Furthermore, in our case, the growth only occurs after the droplet has solidified, which is not the case for the model suggested in Ref. 4 where the droplet retains its liquid character.

The appearance of liquidlike droplets randomly distributed along the length of some of these In nanoparticle-grown NWs [shown in Fig. 3(a)] is interesting but their origin is not known at this point. These structures bear some resemblance to previous results reported on the VLS- and OA-grown NWs where self-oscillating periodic instability mechanism[16] based on the supersaturation/contact angle of the alloy droplet and spheroidization mechanism[17] based on the well-known instability of a cylinder of small diameter under the influence of surface tension were used to explain their occurrences, respectively. Unlike the VLS- and OA cases, however, the location of these liquidlike droplets is asymmetric (seemingly occurring on one side of the NWs) and random. One possible explanation is that they consist of some of the original liquid In nanoparticles which may have been along the path of the growing NW.

The results on the catalyst-free Ge NW growth on porous Si, on the other hand, suggest a nanowire growth mode which involves a solid state nucleation condition right from the beginning, since the melting point of Ge is much too high to form a liquid droplet at the NW growth temperature. The fact that Ge and Si do not form any eutectic also lends support for this argument. It is possible that a size-dependent melting point depression could have occurred, but it would have required a ΔC of 550 °C (where ΔC is defined as the drop of the liquidus in the case of size-dependent melting) for the lower temperature growth, which is much too large. In addition, if that were the case, the solid Ge NWs of diameter <20 nm would not have been found, since they would have all melted prior to any growth. This view would be consistent from the previous report of Wu and Yang[18] where they reported a melting point depression of Ge NWs (30 nm in diameter) inside a carbon nanotube, where Ge NWs only started melting above 600 °C, which suggests a ΔC of 350 °C, which is significantly smaller than that which would be required in our case.

Both of the above results seem to suggest that the NWs are grown from a solid nucleation state (as in Ge NWs) or

once a solid nucleation state has been established (as in In nanoparticle-grown InAs NWs). This in turn suggests that the catalyst-free growth of InAs NWs on a porous Si is also most likely the result of growth from a solid state. Since the elemental ratio of In and As vapors in our closed growth system is not known (unlike molecular beam epitaxy growth system where the control of In and As vapor can be exercised), it is difficult to determine whether or not liquid In droplets could form on the bare porous silicon substrate prior to the InAs NW growth. However, regardless of whether any liquidlike In regions were formed in some local region at the beginning or not, our results suggest that the NWs only grow either from a solid or once a solid nucleation condition has been established.

Lastly, we discuss the role of a rough surface morphology of the porous structure in the growth of the NWs. The results of the InAs NWs on porous Si suggest a correlation between the porosity and the NW formation, with low porosity yielding large-sized nanostructures (and nanobelts) and high porosity yielding NWs. We believe that the NW formation is in part due to the generation of energetically favorable nanometer-sized nucleation sites as a result of nanoscale etch pits/hillocks.[19] For the Ge NWs on a porous Si, the NWs were found everywhere, and we believe this is due to the usage of the high porosity substrate. It is not known at this point why only NWs with diameters <20 nm were found for all cases studied. This will be investigated in future work.

In conclusion, InAs and Ge nanowires were grown on a porous Si substrate without the use of any catalyst. In addition, InAs nanowires were also grown using In nanoparticles. These results suggest that a growth mechanism very different from the VLS is responsible for these growths, involving a solid nucleation state. Thus, in the case of catalyst-free growth of InAs and Ge NWs, we believe that the NWs grew from a solid nucleation state, enhanced by the nanoscale rough surface of the porous Si substrate.

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