# Si-assisted growth of InAs nanowires

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The authors report on the growth of InAs nanowires using nanometer-sized Si clusters in a closed system without any metal catalyst. The growth was performed at 580 °C for 30 min using 1.3 nm thickness of $SiO_x$. It is suggested that the nanowire growth occurred due to highly reactive nanometer-sized Si clusters, which are formed by phase separation of $SiO_x$. The authors have also examined the vapor-liquid-solid (VLS) mechanism under various oxidizing conditions, including different oxygen pressures (200 and 800 mTorr) and oxidized Au–In tip. The results indicate the inhibiting effect of oxygen on the VLS mechanism. © *2006 American Institute of Physics.*
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Two primary nanowire (NW) growth mechanisms have been reported in the literature: the vapor-liquid-solid (VLS) and the oxide assisted (OA). The OA mechanism does not use any metal catalyst, but utilizes the reaction of the suboxide. Previously, NWs such as Ge, GaAs, and Si have been grown by this growth mechanism using GeO,[1] $Ga_2O_3$,[2] and $SiO_x$. From these results, it was suggested that these oxides serve as nucleating centers for subsequent growth of the NWs, but the OA is still not understood.

The VLS, on the other hand, described in detail by Wagner and Ellis[3] and Givargizov,[4] is a growth process that utilizes a liquid metal alloy. Over the years, NWs such as Si (Ref. 4) and InAs (Refs. 5 and 6) have been grown using this mechanism. Recently, a different growth mechanism, namely, the vapor-solid-solid (VSS), where the Au–In tip is solid, was proposed to explain the growth of GaAs (Ref. 7) and InAs (Ref. 8) NWs. In this work,[8] it was reported that Au-catalyzed growth of InAs NWs stopped just above the eutectic point near 450 °C,[9] due to tip melting, but when a 1.3 nm $SiO_x$ layer was added along with the Au catalyst, the growth of InAs NWs at 580 °C was reported. It was suggested that the role of the oxide was to prevent the melting of the Au–In tip, extending the VSS growth process. Our own recent results,[10] however, reported InAs NW growth up to 660 °C (with no $SiO_x$ present), and the Au–In tip continued to retain its liquid feature down to 400 °C. Since our results confirmed the validity of VLS in the InAs system, there is some question as to the real role of the oxide employed in the work of Dick *et al.*[8]

Other results using SiO were also reported, such as the work of Kolb *et al.*,[11] in which SiO evaporation and VLS were combined to grow Si NWs. In this case, the growth model suggested included VLS for the Si NW growth, and the oxide was thought to deposit only around the Si core but not on the Au metal catalyst. Clearly, more research is needed to define the role of oxygen and $SiO_x$ in this growth process. In this letter, we examine the effects of a $SiO_x$ layer

and oxygen on the growth of InAs NWs. Our results show the deleterious effect of oxygen on the VLS growth of InAs NWs, but more importantly, we show that InAs NW growth can be obtained without the use of a metal catalyst, utilizing phase separation of $SiO_x$, where highly reactive nanometer-sized Si clusters act as nucleation/catalyst sites for the wire growth.

The InAs NWs were grown inside a sealed quartz tube (10 mm diameter) in an open tube furnace (10.16 cm diameter), the details of which are discussed elsewhere.[6,10] All the growths were done at 580 °C for 30 min inside the quartz tube initially evacuated to 50 mTorr and torch sealed. In examining the role of oxygen, the quartz tubes were first evacuated to 50 mTorr, backfilled with oxygen to 200 or 800 mTorr, and sealed. The VLS growth was done with 60 nm sized Au nanoparticles using poly L-lysine. For growths involving $SiO_x$, 1.3 nm of $SiO_x$ was deposited onto clean, oxide-free InAs(111)B and Si(111) substrates using a Temescal e-beam evaporator with SiO (99.99%, Kurt Lesker) pellets. The deposition rate was 0.6 Å/s at a base pressure of $1 \times 10^{-6}$ Torr. The grown InAs NWs were analyzed using a LEO SUPRA 55 scanning electron microscope and Hitachi H9000 transmission electron microscope (TEM).

First, the effect of oxygen on the growth of InAs NWs is examined. In Figs. 1(a)–1(c), the NWs grown with the Au catalyst on InAs(111)(5° miscut) at 50 mTorr (no oxygen backfill), 200, and 800 mTorr of backfilled oxygen are shown, respectively. The NWs were all seen terminating with
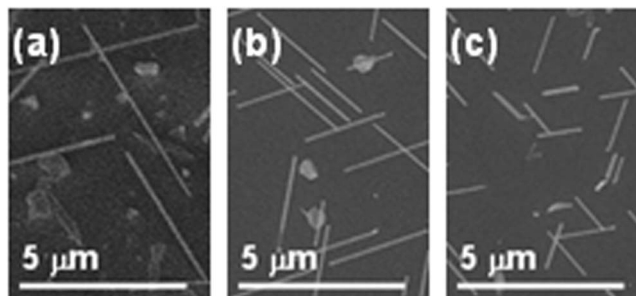


FIG. 1. Growth on InAs(111) with 5° miscut as seen from the top with (a) 50 mTorr (no oxygen backfill); (b) and (c) are with 200 and 800 mTorr of oxygen backfill, respectively.

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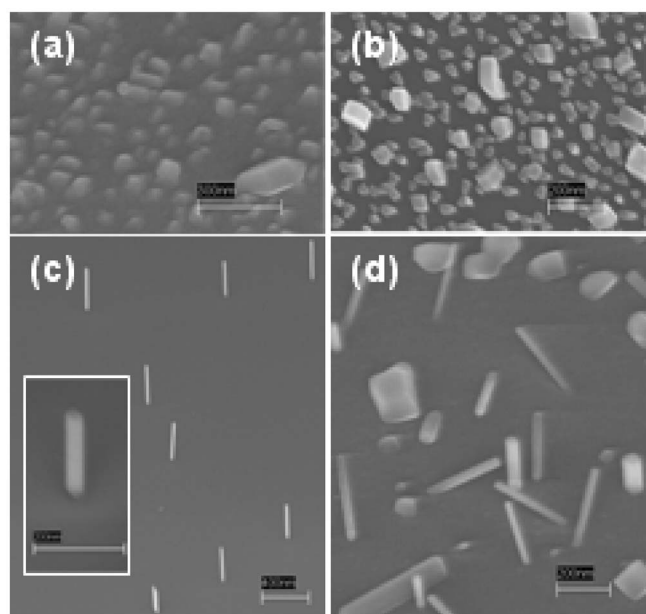
FIG. 2. InAs deposits on (a) InAs(111)B (scale bar: 300 nm) and (b) Si(111) (scale bar: 200 nm) substrates *without* any SiO$_x$ and native oxides. InAs NWs on (c) InAs(111)B (scale bar: 400 nm) and (d) Si(111) (scale bar: 200 nm) substrates *with* 1.3 nm of SiO$_x$. Inset in (c) is the close-up view of the InAs NW.



FIG. 3. Growth terminating points for the (a) VLS and (b) Si-assisted grown NWs. Inset shows the wire end broken off the substrate.

a Au alloy at the tip, as expected for VLS, but the NW length decrease with increasing oxygen content was quite noticeable. We also noticed a proportional increase in the number of Au–In alloy particles that failed to grow into NWs with increasing oxygen level.

To further ascertain the effect of oxygen on the VLS growth, NWs were first grown for only 5 min using a Au catalyst on InAs(111)B substrate. These NWs were then oxidized in air at room temperature for three days, and then grown for an additional 25 min. The quartz tubes were all sealed at 50 mTorr. The NWs grown on InAs(111)B substrate under identical, nonoxidized growth conditions typically yielded a length greater than 2 $\mu$m, but we only observed a small increase in the lengths of the NWs from 5 min (250–300 nm) to an additional 25 min (300–600 nm), which confirms a noticeable growth rate decrease after the oxidation step.

To investigate the effect of SiO$_x$ on the growth of InAs NWs, we performed growths on two types of substrates, InAs(111)B and Si(111), with 1.3 nm of SiO$_x$ (no Au catalyst). We first examined the growth in the absence of any SiO$_x$ (including native oxides) and results of growth on bare InAs(111)B and Si(111) substrates are shown in Figs. 2(a) and 2(b), respectively. The images show variously shaped InAs islands, with the structures on the Si(111) substrate revealing more crystalline features. We next used 1.3 nm of SiO$_x$ and the growth results on InAs(111)B and Si(111) substrates are shown in Figs. 2(c) and 2(d), respectively. Interestingly, the typical diameter of the NWs was about 20–30 nm on both substrates, and the resulting lengths were quite similar. However, while the growth direction of the NWs on the InAs(111)B was along the ⟨111⟩ direction, the growth direction on the Si(111) was random, as shown in Fig. 2(d). In Figs. 3(a) and 3(b), the TEM image of the VLS and SiO$_x$-grown InAs NWs are shown, respectively, at the point of their growth termination. As can be seen, the termi-

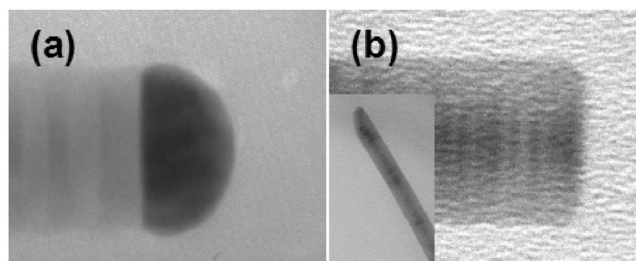nating surface of the SiO$_x$-grown NW is flat and shows the absence of any catalyst particle, unlike the typical VLS (and VSS) grown NWs. The inset in Fig. 3(b) shows the opposite end of the NW (typically fractured), identifying it as the base of the NWs where they had broken off from the substrate during TEM sample preparation. The electron diffraction pattern also revealed SiO$_x$-grown NWs to be single crystal.

Growth was also attempted with only native oxides of InAs (In–O$_x$ and As–O$_x$), where no Au catalyst was used. In this case, a HCl-etched InAs substrate was oxidize in air at room temperature for three days prior to the growth, which results in a native oxide thickness of approximately 1.0 nm.[12] However, unlike in the SiO$_x$ case, we did not find any NW growth on these substrates.

Finally, in order to examine the VLS and the SiO$_x$ growth simultaneously, we deposited Au nanoparticles on existing 1.3 nm SiO$_x$ on the InAs(111)B substrate. In this case, we found that the catalyst-free NWs still grew (as evidenced by the uniform 20 nm diameters and random growth directions), but no Au-mediated NWs were noted in the 30 min growths. However, some were found to grow after longer growth times.

In view of the above results, let us now discuss the effect of oxygen and oxide on the growth of these NWs. First, the oxygen backfill results clearly show the *inhibiting* effect of oxygen on the VLS growth mechanism. Also, the reduced growth rate after the room temperature oxidation of the solid Au–In tips offers additional proof of the deleterious effect of oxygen on the NW growth. Since interdiffusion of Au and In occurs quickly even at room temperature,[13] In in the Au–In alloy would be subjected to surface oxidation[14] and serve as a diffusion barrier for impinging In and As atoms, inhibiting NW growth by the VLS mechanism. This is consistent with our results.

Now, let us consider the effect of an oxide layer on the growth of these NWs. As discussed earlier, no NW growth occurred when the substrate contained a thin In- or As-based suboxide. This would suggest the deleterious nature of oxygen on the resultant NW growth. However, the results were quite different when a silicon suboxide layer was present, where InAs NWs of characteristic 20–30 nm diameters grew. This suggests that the type of oxide may be the determining factor and not the presence of oxygen alone. In the case of a silicon suboxide, the stoichiometry of evaporated SiO$_x$ films is strongly dependent on various evaporation parameters, such as temperature, pressure, and rate of evaporation.[15] Since our deposition conditions were very similar to those used in the previous study,[16] we expect $x$ ≈ 1 for our SiO$_x$ film. It is well known that SiO undergoes a phase separation reaction[15] ($2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$) at higher tem-

peratures ($T > 400\ °C$), yielding nanometer-sized Si clusters.[17,18] We would, thus, expect this phase separation to occur at our growth temperature of 580 °C. Since Zhang *et al.*[19] have reported that Si clusters in the silicon suboxide are energetically very reactive, while $SiO_2$ is quite stable, one would expect that these nanometer-sized Si clusters could enhance the In attachment rate at the cluster surface sites. Since the silicon clusters are in a solid state at 580 °C, the growth of the NWs has to occur via In diffusion through the solid cluster or surface diffusion around the cluster to the growing interface. This suggests a Si-assisted growth mechanism with Si in a solid state. The growth mechanism may seem similar to VSS (or titanium-catalyzed growth[20] of Si NWs), but unlike VSS (or even VLS), not only is the mediating catalyst in Si-assisted growth nonmetallic, but the catalyst particle is also noticeably absent at the point the NW growth terminates. Also, in comparison to the OA growth mechanism, Si-assisted growth does not have any oxygen involved in the growth process.

In our case, an additional factor which enhances our NW growth involves the presence of stable $SiO_2$ surrounding the Si clusters after the phase separation. One can look at this as analogous to growth of NWs using $SiO_2$ masked regions and openings in the mask, where wires nucleate. In this case, enhanced wire growth has been reported as a result of surface diffusion of the growth species from the masked oxide regions to the growing NWs in the openings.[21] In the growth of InAs quantum dots on Si substrate, the success in the selective deposition of InAs on Si using $SiO_2$ mask was similarly attributed to the combination of larger In diffusion coefficient and surface energy of $SiO_2$ ($7 \times 10^{-9}$ cm$^2$/s, 3.83 eV) in comparison to Si ($10^{-20}$ cm$^2$/s, 0.483 eV).[22] Thus, a significant amount of material is provided by diffusion from the surrounding stable oxide and not just from the vapor phase, allowing a faster NW growth.

It should be mentioned that In and Si form a eutectic at ~157 °C,[23] and thus it is possible for a Si–In liquid phase to form, which could act as a metal liquid catalyst for the NW growth by the VLS. However, the at. % of In at the eutectic temperature is ~99.98, which is extremely unlikely. Furthermore, no metal alloy tip has been seen in these NWs, ruling out the VLS mechanism.

In conclusion, the presence of oxygen was found to inhibit the VLS growth mechanism during the NW growth. More importantly, in the case of $SiO_x$, a phase separation at high temperature forms a stable $SiO_2$ and reactive, nanometer-sized Si clusters. It is suggested that these clusters consequently serve as the nucleating/catalyst sites for the growth of InAs NWs with the growth mechanism different from VLS, VSS, and OA.

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