Plasma-enhanced chemical vapour deposition growth of Si nanowires with low melting point metal catalysts: an effective alternative to Au-mediated growth

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Abstract

Au nanoparticles are efficient catalysts for the vapour–solid–liquid (VLS)
growth of semiconductor nanowires, but Au poses fundamental reliability
concerns for applications in Si semiconductor technology. In this work we
show that the choice of catalysts for Si nanowire growth can be broadened
when the need for catalytic precursor dissociation is eliminated through the
use of plasma enhancement. However, in this regime the incubation time for
the activation of VLS growth must be minimized to avoid burying the
catalyst particles underneath an amorphous Si layer. We show that the
combined use of plasma enhancement and the use of a catalyst such as In,
already in a liquid form at the growth temperature, is a powerful method for
obtaining Si nanowire growth with high yield. Si nanowires grown by this
method are monocrystalline and generally oriented in the ⟨111⟩ direction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Catalyst-assisted 1D crystal growth through the vapour–liquid–
solid (VLS [1–3]) mechanism is a widely known mechanism
for growing semiconductor nanowires. The possibility
for nanowire growth with control over wire positioning,
dimensions and directionality opens up the possibility for a
wide range of applications with bottom-up manufacturing at
the nanoscale [4], such as sensors [5], photonics [6] and
microelectronics [7] devices. Nevertheless, the feasibility of
such applications depends on a complete understanding and
control of all the mechanisms governing reproducible whisker
growth with defined characteristics. A large part of this

understanding is still lacking. For example, the vast majority
of the work reported in literature until now makes use of Au
as the metal catalyst, which appears to be a sort of 'universal'
choice for growing the most diverse types of semiconductor
nanowhiskers (e.g. Si, SiGe [8], Ge [9] and III–V [10]). To our
knowledge, only a few studies have shown the feasibility for
VLS growth of Si nanowhiskers mediated by Ga [11], Cu [12],
and vapour–solid–solid (VSS) growth with Al [13] and Ti [14].
All these studies invariably reported a lower efficiency as
compared to Au-catalysed VLS growth. The availability of
alternative catalysts to Au may be enabling for some specific
applications, such as the use of nanowires for Si-based devices.
Au is an undesired metal for Si-based technology. Au diffusion
into Si leads to the creation of deep traps in the Si bandgap, a
killer phenomenon for the minority carrier lifetime [15]. Given

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the small volume of the Si nanowires (roughly in the order of 10^{-16}–10^{-18} cm^3), even a few Au atoms could compromise the performance of the device. It has already been shown that diffusion of Au atoms from the catalyst particle onto the wire surface is a rather favourable process [16]. Therefore, in this study we want to indicate possible alternative metals compatible with Si technology, which can also be efficient catalysts for VLS growth of Si nanowires [17].

The key principle behind the VLS mechanism is the transformation of the solid metal catalyst nanoparticle into a liquid alloy of the catalyst and the semiconductor compound. The liquid particle acts as a privileged site for Si deposition, thanks to the higher sticking coefficient of liquid as compared to solid surfaces [18]. The supersaturation of the droplet, induced by the continuous gas phase supply of Si species, leads to the precipitation of Si nanowhiskers at the interface between the particle and the substrate. Growth is obtained when a steady-state condition is reached between the flux of the silicon through the particle and the precipitation of Si on the substrate.

We will refer here to the time span needed to reach this stage as the 'incubation time' for VLS [19, 20]. Once growth is initiated, the process at the steady state can be broken down into several steps: precursor gas transport to the catalyst particle, gas dissociation at the particle site, sticking and diffusion in the liquid alloy of Si with the metal particle, alloy supersaturation and (1D) precipitation of the Si crystal. The rate limiting step is dependent on the catalyst type and the growth conditions. In conventional CVD growth processes of Si nanowires using silane as gas precursor, the dissociation of the precursor molecule is often reported as the rate limiting step [3].

Au nanoparticles play a key catalyst role in all the above mentioned steps of VLS growth by chemical vapour deposition, thanks to the favourable chemical and physical properties of this noble metal. In particular, Au is an efficient chemical catalyst for silane dehydrogenation/dissociation [21]. Only few metals show this property [22], which poses stringent restrictions on the spectrum of possible catalysts. With the use of plasma enhancement upon CVD growth, pre-dissociated Si species are transported to the substrate and the catalyst. Therefore, the catalytic dissociation of the precursor molecule is not required and the catalyst choice can be broadened beyond the class of chemical catalysts. This way, the process balance is shifted away from a source-limited regime and the slowest step of the VLS mechanism (either the Si diffusion into the catalyst particle or the precipitation from the supersaturated alloy) will become the rate limiting step. A first example of Si nanowire growth assisted by plasma enhancement has been shown by Hofmann *et al* [23] with Au particles. This was in 2003, but this avenue has been given only minor attention in the meantime. One reason could be the fact that nanowire growth in the plasma-enhanced regime suffers from the competition with parasitic deposition of amorphous silicon (a-Si). Later on, Sharma and Sunkara showed Si nanowire growth with plasma enhancement from Ga molten pools [24]. Growth from large pools may not sound technologically appealing, as it requires post-growth manipulation and placement of the single wires. Nevertheless, continuing on the same research line, we will show that the combined use of plasma enhancement with a low melting point metal catalyst is an effective alternative route to Au-mediated growth of Si nanowires. We will also point out the importance of a prompt activation of the catalyst particles (i.e. a short incubation time for the VLS mechanism) for obtaining Si nanowire growth with high yield.

2. Experimental details

In this work we compare Al and In nanoparticles as catalyst materials, both shallow impurities and thus possible doping elements for Si. Early growth trials using In as catalyst with conventional chemical vapour deposition technique were not successful [3].

Indium nanoparticles with a diameter range of 40–80 nm were electrodeposited on (001) Si from an aqueous solution of InCl$_3$ (0.05 M), KCl (0.2 M) and HCl (0.005 M) at a constant current density of 10 mA cm^{-2} [25]. Prior to In deposition, the Si surface was cleaned in 2 wt% hydrofluoric acid. Al nanoparticles were formed through *ex situ* physical vapour deposition of 10 nm thin films, and subsequent agglomeration induced by exposure to H$_2$ plasma. The plasma exposure was performed *in situ* with growth, at the same temperatures chosen for the growth processes. The final Al particles size was in a similar range as for the In particles. Al nanoparticles were formed either directly on (001) Si substrates or on top of 50 nm thick SiO$_2$ and Si$_3$N$_4$ layers on Si.

Nanowires were grown in a cold-wall plasma-enhanced chemical vapour deposition (PE CVD) system (PlasmaLab100 by Oxford Instruments). The top electrode of the system is provided with a shower head through which the gases flow before reaching the chamber and is coupled to a radio-frequency (RF) power generator (13.56 MHz). The Si substrates are placed on the bottom electrode, which is grounded and placed at a 20 mm gap distance from the top electrode. All growth processes were carried out for 10 min simultaneously on samples with different catalysts placed on the same carrier substrate, for direct comparison. H$_2$ plasma treatments (200 W RF power for 20 min) were performed *in situ* prior to the growth process on all samples, with a twofold purpose: (1) particle formation through agglomeration of the Al film and (2) surface cleaning by chemical reduction of the surface oxides present on the substrate and the metal particles. SiH$_4$ was used as source gas for Si nanowire growth, mixed with Ar and/or H$_2$. Conditions of low plasma power (5 W) and low chamber pressure (500 mTorr) are used for nanowire growth. Gas flow ratios and process temperatures are variable parameters. Low silane partial pressures (0.12–0.25 Torr) were used for the experiments. The process temperature is controlled through a thermocouple connected to the bottom electrode. The substrate temperature can be 10–30 °C lower than the set point, depending on the process conditions.

The Al–Si phase diagram is a eutectic type, as for Au–Si. The bulk Al–Si system has a eutectic temperature of 577 °C, roughly 100 °C lower than the melting point of Al [26]. On the other hand, In is a low melting point metal, and the eutectic temperature of the In–Si binary system coincides with the melting temperature of indium, around 157 °C [26]. Also note that the In–Si eutectic alloy exhibits an extremely low Si solubility ($\sim 10^{-4}$ at.% Si) and a steep liquidus line, such that the liquid alloy is promptly supersaturated with Si in a
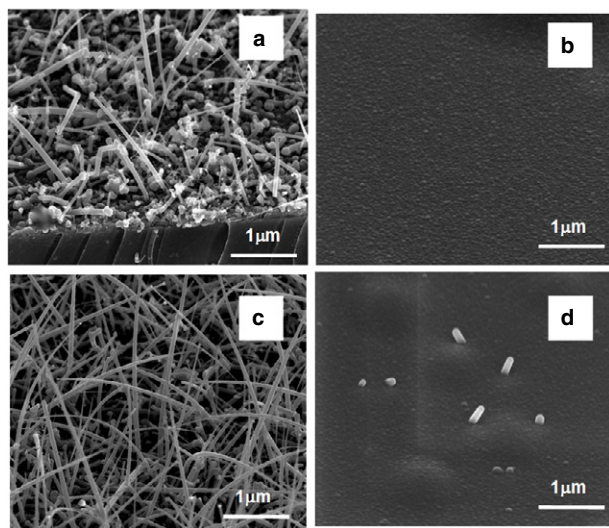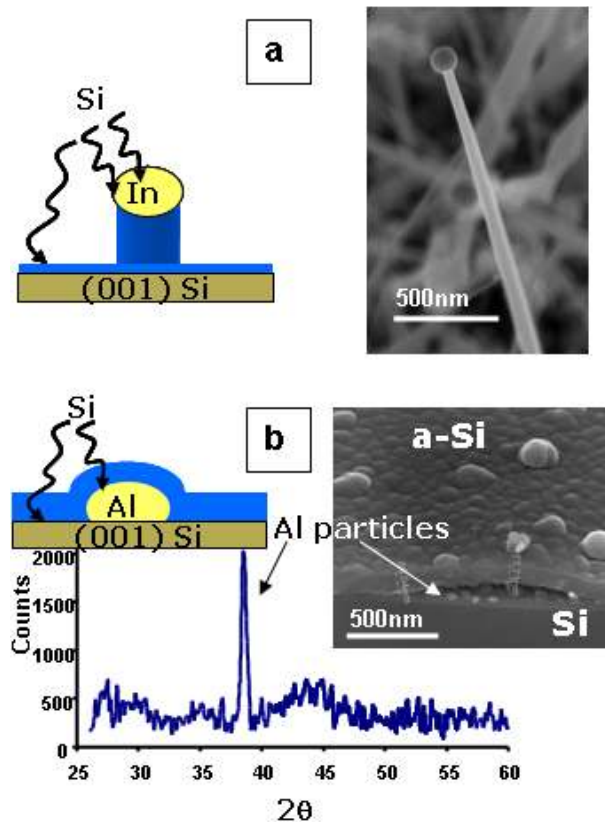
Figure 1. Growth of Si nanowires at 500 °C from In (a) and Al (b) catalysts on (001) Si from a SiH$_4$/Ar 1:1 mixture. The Al catalysts are not active at this temperature, whereas some growth from Al is observed when the growth temperature is 600 °C (d), above the Al–Si eutectic point. Nanowires grown from In catalysts at 600 °C (c) are of better quality than those grown at 500 °C.

wide range of temperatures (at least up to 800 °C). The Al–Si eutectic composition shows a higher Si content of about 13 at.% Si. In addition, the Al–Si liquidus line has a smaller slope versus Si concentration as compared to the In–Si system. This indicates that, for temperatures above the Al–Si eutectic point, the concentration needed to achieve supersaturation with Si in the liquid alloy can be considerably higher than the eutectic Al–Si composition.


Figure 2. Schematic explanation of the different growth behaviour with In and Al catalyst particles. Since the In particles are already liquid at the growth temperature, the incubation time is much shorter as compared to Al, and wire growth is initiated before the particles are buried underneath an a-Si layer (a). X-ray diffraction analysis on the buried Al particles shows no peaks from c-Si, indicating that the deposited layer is exclusively amorphous (b).

3. Results and discussion

Figure 1 shows scanning electron microscope (SEM) micrographs (45°-tilted) comparing PE CVD growth processes with a 1:1 SiH$_4$/Ar mixture with In and Al nanoparticle catalysts on Si at 500 °C and 600 °C. At a temperature of 500 °C Si nanowire growth is observed only with In catalysts (figure 1(a)). As shown in figure 1(b) and in the cross section in figure 2(b), the Al particles are buried under a Si layer about 110 nm thick. An x-ray diffraction analysis on the same sample yields only a peak near $2\theta = 38.5°$, corresponding to diffraction from Al(111) lattice planes (figure 2(b)). The absence of Si diffraction peaks indicates that the Si layer covering the catalysts is amorphous. From figures 1(a) and (b) it follows that the growth mechanism at 500 °C is active for In but not for Al. Note that the growth process is carried out at a temperature below the eutectic temperature of Al–Si (577 °C), so no VLS growth is expected for Al. Si nanowire growth (thermal CVD) with Al catalysts below the Al–Si eutectic point has been reported through a vapour–solid–solid (VSS) mechanism [13], but is not observed under our experimental conditions (PE CVD). The most probable reason for this is that growth through a VSS mechanism is several orders of magnitude slower than growth through VLS, as its rate is strongly limited by the slow diffusion kinetics of Si through

the solid Al particle. Hence, the parasitic deposition of a-Si inhibits VSS growth in the case of PE CVD.

An important observation is that the deposition of a-Si onto the Si substrate with In catalysts is at least ten times slower as compared to the deposition on bare Si substrates or samples with inactive catalysts (Al in this case). This fact indicates that the In particles act immediately as the preferred site for Si deposition. This is because the catalyst is already in liquid form from the start without need for alloying with Si, as the process temperature is higher than the melting temperature of indium. The activation of the VLS mechanism is thus prompt, thanks to the higher sticking coefficient of liquid surfaces and the fast Si diffusion through the already liquid particle. In addition, the very low Si concentration required in the In particle to achieve supersaturation of the liquid alloy (only slightly above 10^{-3} at.%, In–Si diagram [26]), further helps in establishing quickly an equilibrium between the flux of incoming Si atoms in the vapour phase and the precipitation of the Si nanowhisker.

Growth with In particles at 600 °C (figure 1(c)) shows higher wire density and growth rate (as high as 1 μm min^{-1}) as compared to growth at 500 °C. Also, the shape of the wires appears more regular and free of kinks. Conversely, only marginal growth is observed at 600 °C with Al catalysts
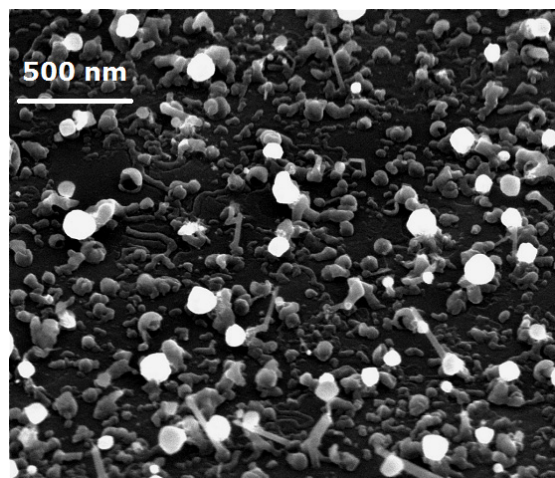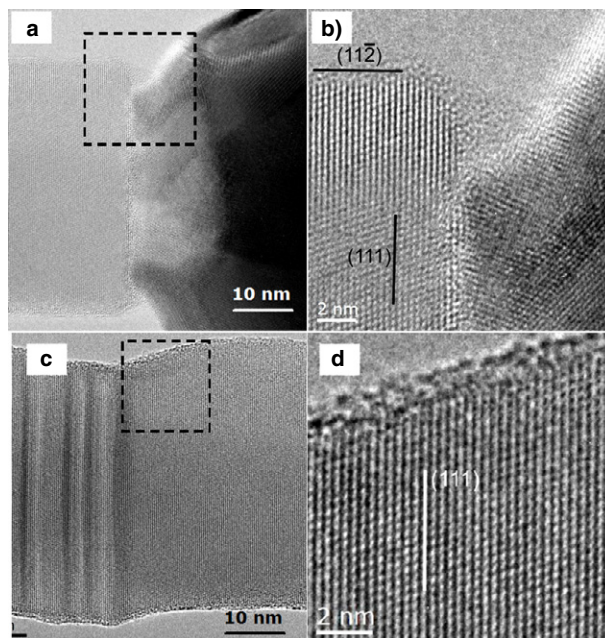
Figure 3. The micrograph shows our best attempt to grow Si nanowires with In on Si without plasma enhancement. The process was performed at 600 °C with undiluted SiH$_4$ at $P = 1.5$ Torr. Only marginal growth is observed.


Figure 4. TEM micrographs of a typical Si nanowire grown using In particles with plasma enhancement at 600 °C, as for figure 1(c). Figures (a) and (b) show the tip of the nanowire, whereas (c) and (d) show a central segment of the wire. The high resolution micrographs indicate that the wire is monocrystalline with $\langle 111 \rangle$ growth direction and {112} facets. Twinning defects are present (c).

(figure 1(d)), although the process takes place above the Al–Si eutectic temperature. Most of the particles are not activated fast enough for VLS, and appear again buried underneath an amorphous layer. The activation of the VLS mechanism for growth with Al particles needs a longer incubation time than growth with indium. The Al particles are in a solid state at temperatures below 660 °C, therefore, we have to rely on the alloying of Al with Si to obtain a liquid particle. This is possible above the eutectic temperature of the Si–Al system, but the kinetics for the Si diffusion through solid Al is slow, leading to a long incubation time (roughly between 1 and 2 min in the observed conditions) for VLS growth. A rough estimation of the diffusion rates of Si in Al from the activation energies and pre-exponential factors reported in [27] yields a value around 1.2×10^{-12} m^2 s^{-1} for diffusion at 600 °C through solid fcc Al. This is indeed three orders of magnitude slower that diffusion of Si through liquid Al (about 2×10^{-9} m^2 s^{-1}). Diffusion of Si through liquid In is expected to be roughly in the same order of magnitude as diffusion through liquid Al [28], thus considerably faster than through a solid catalyst particle.

As long as VLS growth is not initiated, the Si species supplied in the vapour phase tend to deposit in the form of an amorphous film covering the catalyst particles. No nanowire growth is started when the deposition rate of a-Si is high enough to completely bury the catalysts within the incubation time span of the particles for VLS.

The behaviours observed for In and Al catalyst particles are schematically shown in figures 2(a) and (b), respectively. Nanowire growth with In particles can be initiated with only minimal a-Si deposition in between the catalysts, as a result of the prompt activation of the VLS mechanism. Conversely, the incubation time for VLS with Al particles is too long compared to the deposition rate of a-Si and the particles are buried before any growth can be started. The micrograph in figure 2 also shows the rather spherical shape of the indium catalysts on the tip of a Si nanowire.

Note that the use of plasma enhancement upon growth is another important point for obtaining high yield growth of Si

nanowires with In. Growth trials in thermal CVD conditions exploring silane partial pressures up to 6 times higher than the partial pressures used with plasma enhancement in figure 1, did not yield satisfactory results. Figure 3 shows an example of poor thermal CVD growth with In catalysts at 600 °C with undiluted SiH$_4$ and a chamber pressure of 1.5 Torr.

Figure 4 shows transmission electron microscope (TEM) micrographs of the nanowires grown with In and plasma enhancement at 600 °C (conditions as for figure 1(c)). Figures 4(a) and (b) show the tip, and figures (c) and (d) show a central segment of a typical nanowire. The high resolution micrographs ((b) and (d)) clearly show monocrystalline Si with $\langle 111 \rangle$ growth orientation. Twinning defects are sometimes observed, as shown in the left area of figure 4(c). In some cases also other orientations than $\langle 111 \rangle$ are found, mainly for the wires with the smallest diameters (around 30 nm). The different orientation for small diameter wires is in agreement with earlier reports [29].

Figure 4(b) focus on the 'triple point', where, upon growth, the liquid phase from the catalyst, the solid phase of the Si wire and the gas phase of the ambient meet. This should also be the point with highest driving force for precipitation of the Si nanowire. Note the high contact angle between the catalyst particle and the Si wire, a consequence of the low mutual solubilities of In and Si.

So far, we have shown that the incubation time for VLS is a major constraint in plasma-enhanced CVD regime. Next, we will show that growth yield with Al can be improved by decreasing the deposition rate of amorphous Si. This allows more time for the 'solid' particle to reach the necessary Si concentration to form a supersaturated liquid alloy. We chose
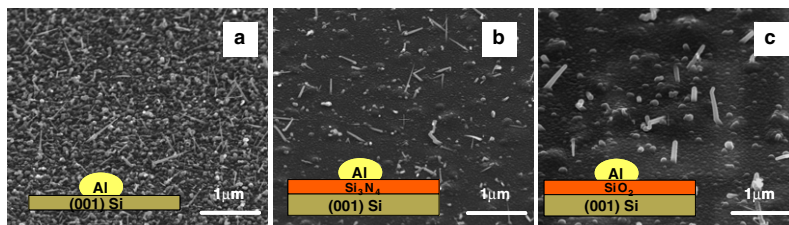
Figure 5. The addition of H$_2$ in the SiH$_4$/Ar gas mixture (2:1:1) enables growth of Si nanowires with Al catalyst on Si (a) at 600 °C. However, only marginal growth is observed with the same conditions when Al is deposited on top of a SiO$_2$ or Si$_3$N$_4$ layer on Si ((b) and (c), respectively).
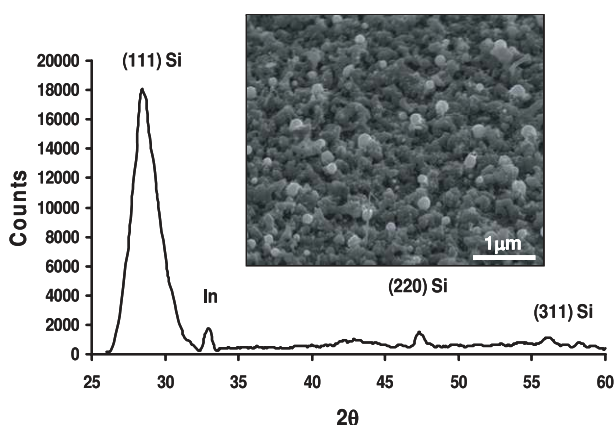
Figure 6. X-ray diffraction analysis on In particles after growth experiments at 300 °C, together with a SEM micrograph indicate a 2D growth of a polycrystalline Si layer, where the In particles are floating on top of the poly-Si.

to do this through the addition of H$_2$, as it has a twofold action: it promotes etching of a-Si [19, 30] and hampers a-Si deposition through the formation of Si–H terminations on the surface of the Si substrate [31].

The a-Si deposition rate on bare Si at 600 °C is almost halved (from 11 to 6 nm min^{-1}) upon addition of H$_2$ gas in the SiH$_4$/Ar mixture in a 2:1:1 ratio. Results of nanowire growth with Al catalysts on Si in such conditions are shown in figure 5. This time, nanowire growth is observed also with Al catalysts (figure 5(a)), although the nanowire yield is still lower than for In particles (not shown). The wire length is substantially shorter as well, partly as a result of the longer incubation time for the VLS activation of Al catalysts.

Under the above conditions which yield nanowire growth with Al directly on Si substrates, only marginal growth is observed when Al particles are deposited on SiO$_2$ or Si$_3$N$_4$. In the latter case most of the particles appear once again buried underneath an amorphous Si layer (figures 5(b) and (c)). This confirms the importance of the incubation time. When the catalyst particle is deposited on Si, the metal–silicon alloying process can already start during the pre-growth thermal treatments, with the Si being supplied directly from the substrate [32]. When a foreign layer is deposited between the catalyst particles and the Si substrate, the pre-growth alloying is suppressed and the activation of the VLS mechanism is further delayed.

In figure 6 we show that a growth mechanism with In particles analogous to VLS can take place also at temperatures as low as 300 °C (still above the melting temperature of In), as demonstrated by the In particles floating on top of a granular Si layer. Nevertheless, the precipitation of Si happens in a rather uncontrolled fashion, leading to the 2D growth of a polycrystalline Si structure with preferential (111) grains, instead of 1D isolated monocrystals. These results indicate that activation of VLS growth is not the only requirement for 1D nanowhisker growth. Most of the literature reports Si epitaxial nanowire growth with Au catalysts above at least 450–500 °C, i.e. well above the Au–Si eutectic temperature [3, 33]. The temperature threshold requirement for nanowire growth is probably linked to a balance between the precipitation rate from the particle and the diffusion length of Si atoms at the catalyst/substrate interface to arrive at the appropriate lattice position and initiate a 1D epitaxial growth [34, 35]. Phenomena like unfavourable wetting of the substrate by the liquid catalyst particle or premature disordered phase separation could also lead to effects such as the one shown in figure 6.

We have demonstrated that the incubation time for the activation of the catalyst particle for the VLS mechanism is a critical parameter for initiating nanowire growth with high yield in plasma-enhanced CVD regime. The incubation time for the growth of catalyst particles which are solid at the growth temperature is too long to favourably compete with the parasitic a-Si deposition. Au catalyst particles, being in a solid form until a Au–Si alloy is formed at the temperatures of interest (the melting point of Au is at 1063 °C), could show similar restrictions as Al for growth when the conditions are moved away from a source-limited regime. Incubation times ranging in the order of several tens of seconds for growth of Si nanowires mediated by Au have been reported, depending on conditions such as temperature and gas phase pressure in thermal CVD processes [12, 3]. Moreover, it is currently not completely understood yet how specific conditions such as the concentration gradient of Si from the gas to the liquid phase, and the concentration gradient within the liquid phase affects the incubation time. Kalache *et al* [12] modelled the incubation time for VLS activation with solid particles as the movement of the liquid–solid interface through the catalyst particle towards the substrate. They report that the diffusion kinetics of Si through the solid catalyst can be described by a typical Arrhenius behaviour where the pre-exponential factor of the diffusion coefficient of Si in the solid particle is modulated by the Si concentration gradient in the liquid. Further investigations in this direction would be extremely useful to predict the most appropriate growth conditions in those cases where low melting point metals cannot be used.

4. Conclusions

We have shown that the use of a deposition technique where Si is supplied in dissociated species to the substrate (i.e. plasma-enhanced CVD but also methods based on Si sublimation) broadens beyond Au the choice of metal candidates as catalysts for VLS nanowhisker growth. However, the incubation time to initiate the VLS growth process becomes a crucial parameter when the growth process is no longer source-limited. No nanowire growth is initiated when the rate of amorphous Si deposition is high enough to bury the catalyst particles during the incubation time. It is shown that a prompt VLS activation is obtained by using metal catalysts which are already liquid at the chosen growth temperature. The incubation time for a solid metal catalyst is drastically longer than for a liquid droplet, as a result of the slow diffusion kinetics of the Si through the solid particle. We have shown that indium, as a low melting point metal, is a good candidate for VLS growth of Si nanowires with high yield for microelectronics applications.

Besides In, other eligible low melting point metal catalysts for Si semiconductor technology should be identified among the elements from the III, IV and V groups, as they should be either electrically neutral in Si or induce only shallow shifts in the Si bandgap [15]. For example, Ga, Bi, and Sn are low melting point metals with limited Si solubility and do not form intermediate compounds with Si. As such, they are additional promising candidates as catalysts for the growth of Si nanowires.

Acknowledgments

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