Alternative catalysts for Si technology -compatible growth of Si nanowires

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ABSTRACT

The use of Au nanoparticles as catalysts for growth of Si nanowires poses fundamental reliability concerns for applications in Si semiconductor technology. In this work we show that the choice of catalysts can be broadened when the need for catalytic precursor dissociation is eliminated. However, the requirements for selective deposition in a gas phase transport –limited regime become stringent. When competing deposition of amorphous Si can bury the particles faster than the incubation time for VLS growth, no nanowire growth will be initiated. We show that the use of a catalyst such as In, already in a liquid form at the growth temperature, is effective. Therefore, the choice of VLS catalysts among the low melting point metals from the III, IV and V groups is suggested.

INTRODUCTION

Catalyst –assisted 1D crystal growth through the Vapour-Liquid-Solid (VLS [1,2,3]) mechanism is a widely demonstrated method for growing semiconductor nanowires. Nevertheless, a complete understanding and control of all the mechanisms governing precise and reproducible whisker growth with defined characteristics is still lacking. Until now, the vast majority of the work reported in literature 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 [4], Ge [5] and III-V [6]). In the case of III-V and II-VI compound semiconductors, nanowire growth at moderated temperatures has been demonstrated from a metal catalyst that is also one of the compound elements [7]. A few sporadic studies have assessed the feasibility for VLS growth of Si nanowhiskers mediated by Ga [8], Cu [9], and Vapour-Solid-Solid (VSS) growth with Al [10] and Ti [11]. All these studies reported a lesser efficiency as compared to Au –catalysed VLS growth. Early growth trials using In catalysts with Chemical Vapour Deposition technique were not successful [].
The availability of alternative catalysts to Au may be enabling for some specific applications, i.e. the use of nanowires for Si –based devices. Au is an unfavourable metal for Si –based devices, since Au diffusion into Si would lead to the creation of mid- band gap states, and be a performance killer by reducing the minority carrier lifetime [12]. Therefore, in this study we focus on possible alternative metals compatible with Si technology, which could also be efficient catalysts for VLS growth of Si nanowires [13]. The general requirements, the critical mechanisms and related shortcomings that can be encountered with non –Au catalyst materials are pointed out. We also show that what

ultimately determines the eligibility of a given metal catalyst is the thermodynamic behaviour of the metal-Si alloy, together with the kinetic factors affecting the activation of the catalyst particle for VLS.

Growth process by Chemical Vapour Deposition and thermodynamics of VLS

The VLS growth of nanowires by chemical vapour deposition (CVD) 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, supersaturation and (1D) precipitation of the Si crystal.

Au nanoparticles play a key catalyst role in almost all the above mentioned steps of VLS growth by chemical vapour deposition, due to the favourable chemical and physical properties of the noble metal. In particular, Au is also an efficient chemical catalyst for silane dehydrogenation/dissociation [14]. This property is common to a few metals [15], however it is not strictly necessary for VLS growth.

In this study we want to focus exclusively on the catalyst requirements enabling nanowhisker growth by the VLS mechanism. Therefore, we use plasma enhancement for obtaining efficient precursor gas dissociation and bringing our Si deposition conditions as much as possible towards a gas phase transport –limited regime. In such way, the requirement for chemical catalysis by the nanoparticle is not longer necessary and the spectrum of the possible catalysts can be broadened beyond the class of chemical catalysts.

However, nanowire growth in this regime competes with a parasitic deposition of amorphous, a-Si. In this case the requirements for a selective Si deposition become stringent, and a prompt activation of the catalyst nanoparticle for VLS growth is crucial. In the next sections, we will point out that both thermodynamic and kinetic parameters for forming a supersaturated liquid alloy of Si and the catalyst material play a fundamental role in the incubation time for the activation of the VLS mechanism.

EXPERIMENTAL DETAILS

In, Al and Ti nanoparticles were used as catalysts for growth of Si nanowires on (001) Si. The Al-Si system has a eutectic temperature of 577°C, about 100°C lower than the melting point of Al [16]. The eutectic temperature of the In-Si binary system is considerably lower and coincides with the melting temperature of Indium, around 157°C [16].

Indium nanoparticles with a diameter range of 40-80nm were electrodeposited from an aqueous solution of $InCl_3$, KCl and HCl at a constant current density. Prior to In deposition, the Si surface was cleaned in 2 wt% hydrofluoric acid. Al and Ti nanoparticles were formed through physical vapour deposition of 10nm thin films and subsequent agglomeration induced by exposure to H_2 plasma, at the same temperatures chosen for nanowire growth. The final particles size was in a similar range as for the In particles. Al nanoparticles were formed either directly on the Si substrate or on top of 50nm thick SiO_2 and Si_3N_4 layers on Si.

Nanowires are grown in a cold –wall Plasma –Enhanced Chemical Vapour Deposition (PE CVD) system PlasmaLab 100 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 generator (13.56 MHz). The Si substrates are places on bottom electrode, which is grounded and placed at a 20mm gap distance from the top electrode. SiH_4 was used as source gas for Si nanowire growth, mixed with Ar and/or H_2. Conditions of low plasma power (5W) and low chamber pressure (500mTorr) are used for nanowire growth. Gas flow ratios and process temperatures are variables. The process temperature is controlled through a thermocouple connected to the bottom electrode. The substrate temperature may be 10 to 20°C lower than the set point, depending on the process conditions.

Growth processes were carried out for 10 minutes simultaneously on samples with different catalysts placed on the same carrier substrate, for direct comparison. Hence, the H_2 plasma treatments are performed in-situ for 20 minutes 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.

RESULTS AND DISCUSSION

PE CVD growth processes with a 1:1 SiH_4/Ar mixture at 500°C and 600°C with either In or Al nanoparticle catalysts were compared. At a temperature of 500°C, Si nanowire growth is observed only with the In catalysts, while all Al particles are buried under a Si layer about 110nm thick. As the growth process is carried out at a temperature below 577°C, the eutectic temperature of Al-Si, no VLS growth is indeed expected for Al. Possibility for Si nanowire growth with Al catalysts without a liquid phase through the Vapour-Solid-Solid (VSS) mechanism has been reported [], but in our experimental conditions we do not observe growth at temperatures below the Al-Si eutectic point. The same statement is valid for Ti: we did not observe any growth in the temperature range we investigated, which is always below the Si-Ti eutectic [16]. The growth rates for VSS growth are most probably too unfavourable to compete with a-Si deposition by PE CVD. **Figure 1** shows scanning electron microscope (SEM) micrographs (45° tilted) comparing growth at 600°C. Growth with In particles at 600°C (**Figure 1 a**) shows higher wire density and growth rate (as high as 1μm per minute) as compared to growth at 500°C. Also, the shape of the wires appears less defective, free of kinks. On the other hand, only marginal growth is observed at 600°C with Al catalysts (**Figure 1 b**), 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.

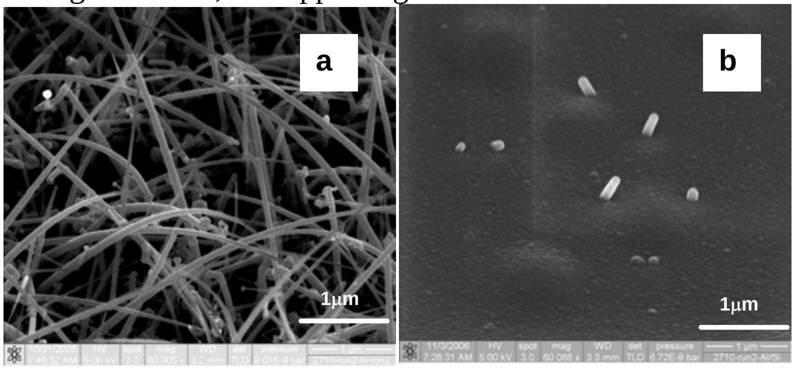

Fig.1 Growth of Si nanowires at 600°C from In (a) and Al (b) catalysts from a SiH_4/Ar 1:1 mixture. Most of the Al catalysts are not active for growth and are buried underneath an a-Si layer, although the growth temperature lies above the Al-Si eutectic. Nanowires grown from In catalysts at 600°C show high yield and are of better quality than those grown at 500°C.

The deposition of a-Si onto the substrate with In catalysts is at least ten times slower as compared to the deposition on bare substrates or samples with inactive catalysts (Al). This fact indicates that the In particles can immediately act as preferred site for Si deposition. The main reason is that the catalyst is already in liquid form when the growth process is started, as the process temperature is higher than the melting temperature of indium. The activation of the VLS mechanism is thus prompt, thanks to the fast Si diffusion through the already liquid particle. Note that a Si concentration in the particle only slightly above 10^{-8} at% is sufficient to drive the liquid alloy into supersaturation [16].

The activation of the VLS mechanism with Al particles is more difficult than for 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. The kinetics for the Si diffusion through solid Al is expected to be slow, leading to a long incubation time until the Al particle is transformed into a Al-Si liquid alloy. 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. This effect leads to the complete poisoning of the catalyst before nanowire growth can be started.

Since the incubation time for VLS is a major limitation, improved yield can be achieved by decreasing the deposition rate of amorphous Si. This would allow more time for the particle to reach the necessary Si concentration to form a supersaturated liquid alloy. Upon addition of H_2 gas in the SiH_4/Ar mixture in a 2:1:1 ratio, the a-Si deposition rate at 600°C is halved (from 11nm min^{-1} to 6 nm min^{-1}). The addition of H_2 has a twofold action: it promotes etching of a-Si [17,18] and also hampers a-Si deposition through the formation of Si-H terminations on the surface of the Si substrate [19]. Results of nanowire growth with the addition of H_2 are shown in **Figure 2**. This time the VLS growth is observed also with Al catalysts (**Fig.2b**), although the nanowire yield is still lower than for In particles (**Fig. 2a**). The wire length is substantially shorter as well, mainly a result of the long incubation time for the VLS activation of Al catalysts. Note that the boundary conditions for VLS growth mediated by Al are rather restrictive. Under the same conditions yielding growth with Al directly on Si, marginal growth for Al particles deposited on SiO_2 or Si_3N_4 is observed. In the latter case most of the particles appear once again buried underneath an amorphous Si layer (**Fig.2c**). The process of alloying of the catalyst with Si typically starts already during the pre-growth thermal treatments, with the Si supplied directly from the substrate [20]. When the catalyst particles are not deposited directly on Si this pre-growth alloying is suppressed, and the incubation time for VLS activation is indeed expected to be longer.

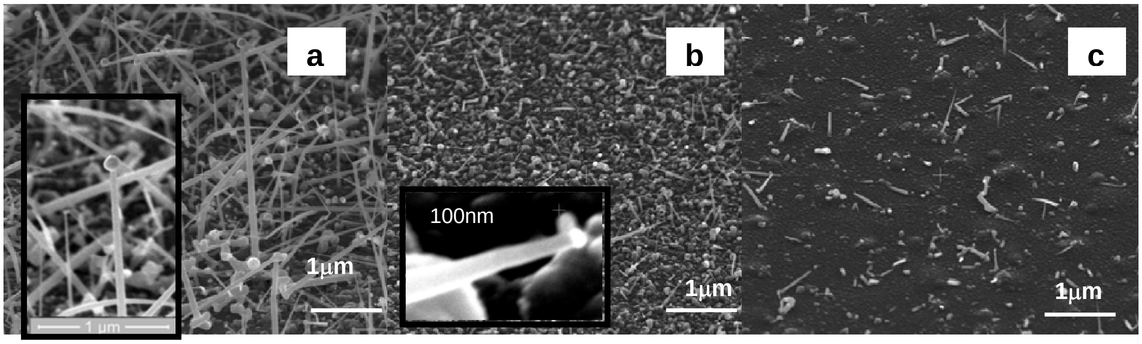

Fig.2 The addition of H_2 in the SiH_4/Ar gas mixture (2:1:1) enables growth of Si nanowires with Al catalyst on Si (b). Growth mediated by In (a) still shows higher wire density and growth rate. The insets show the In (a) and Al (b) particles with higher magnification. When Al is deposited on top of a SiO_2 or Si_3N_4 layer (c), only marginal growth is observed.

We have shown 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 a gas phase transport –limited regime. Therefore, the use of metal catalysts already in a liquid form at the chosen temperature for nanowire growth, i.e. low melting point metals, is recommended for a prompt activation. The incubation time for catalyst particles that are in a solid phase at the growth temperature is dramatically slower [21]. Kalache et al.[] modeled the incubation time for VLS activation with solid particles as the movement of the liquid-solid interface through the catalyst particle to reach the substrate. They reported that the diffusion kinetics of Si through the solid catalyst responsible for this incubation time 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.

Au catalyst particles, being in a solid form until a Au-Si alloy is formed for temperatures of interest (the melting point of Au is at 1063°C), could show similar restrictions as Al for growth in a gas phase transport –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 of conditions such as temperature and gas phase pressure in thermal CVD processes [,22]. Moreover, at the moment it is not yet completely established 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 would affect the incubation time. Further investigations in this direction would be extremely useful to predict the most appropriate growth conditions depending on the chosen metal catalyst.

CONCLUSIONS

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 evaporation) broadens beyond Au the metal candidates efficient catalysts for VLS nanowhisker growth. In this way, the requirement for chemical catalysis is eliminated, and only the kinetic and thermodynamic requirements linked to the formation of a liquid metal-Si alloy are left. Nevertheless, the incubation time to initiate the VLS growth process is a crucial parameter. As long as the VLS growth is not initiated there is no selective deposition of Si. Consequently, no nanowire growth will be possible if 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. Indeed, the incubation time for a solid catalyst metal is drastically longer than for a liquid droplet, as the result of the slow diffusion kinetics of the Si through the solid particle. In addition, our experiments confirm that liquid particles do exhibit higher sticking coefficient than solid surfaces.

Since nanowire growth temperatures below 600°C are preferred for microelectronics applications, low melting point metals with metal-Si phase diagrams of the eutectic type are recommended. Besides In, other favourable metal catalysts fulfilling compatibility requirements with Si semiconductor technology are several elements from the III, IV and V groups, for example Ga, Bi, and Sn. Also alloys of such metals could be considered as catalysts. From a thermodynamic point of view, all these metals show limited Si solubility and do not form intermediate compounds with Si.

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