Aspects of Silicon Nanowire Synthesis by Aluminum-Catalyzed Vapor-Liquid-Solid Mechanism

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Abstract—**The VLS growth method was first developed in the 1960s, but recently there has been a renewed interest in this method for growing nanowires of varying compositions. Many of these studies have investigated silicon nanowire growth catalyzed by metallic eutectic particles, generally gold (Au). This technique consists of the absorption of a source material (e.g silane) from the gas phase into an Au liquid droplet. When this liquid alloy becomes saturated, a silicon solid precipitate is generated and serves as a preferred site for further deposition. While the gas flow is maintained, the source material diffuses through the molten Au-Si droplet and grows epitaxially at the liquid-solid interface.**

To incorporate these nanostructures into microelectronic devices, the nanowire growth mechanism has to be fully compatible with the standard integrated circuit techniques and materials. We are investigating the use of aluminum (Al) as the catalyst particle for VLS growth. Aluminum is a standard metal in silicon process lines and seems to be an interesting alternative for silicon nanowire growth. Nevertheless, using aluminum as catalyst for nanowire growth is not straightforward. This paper treats some of the difficulties that have been encountered.

Keywords— **silicon nanowire; phase diagram; vapor-liquid-solid technique; metallic catalyst**

I. INTRODUCTION

One-dimensional nanostructures such as carbon nanotubes and semiconducting nanowires are expected to play to key-role not only for testing of fundamental phenomena as well as for potential nanotechnology applications. Due to their potential for the fabrication of nanoscale devices, semiconducting nanowires have been the object of intensive study over the past few years. Typically, these nanostructures are cylindrical single crystals with a diameter of 10 nm – 100 nm and a length of several microns. The ability to predictably control their properties makes nanowires particularly promising to be used as a building block for the next generation of nanoscale devices. Indeed, the flexibility of growing parameters makes it possible to combine different materials and doping profiles in order to form p/n junctions[1], Schottky diodes[2], or single electron transistors[3]. In addition, the large surface to volume ratio of semiconducting nanowires makes them attractive for sensor applications.

Several nanowire growth mechanisms have been developed, such as template-assisted synthesis, laser ablation[4], chemical vapor deposition[5] (CVD), electrochemical deposition[6], or vapor-liquid-solid (VLS) approach[7]. By using these different techniques, a large variety of semiconducting nanowires have been reported; indium phosphate[8], gallium nitride[2], germanium[5] or silicon[9] nanowires have been fabricated over the past few years. Most of the recent successful semiconducting nanowire growth is based on the VLS technique.[10,11] This crystal synthesis method is well known. It was first proposed by Wagner and Ellis[12] in 1964 for the growth of silicon whiskers with diameters from one hundred nanometers to hundreds of microns, and then described in detail by E. I. Givargizov[13] in 1975. But due to the recent need for systematic nanostructure synthesis and the progress in the formation technique of metal nanosize particles, there is a renewed interest in the VLS technique.

Metallic nanoparticles play a key-role in the VLS process. Nanowires obtained by such a crystal growth mechanism are catalyzed by a metal eutectic nanodroplet. Due to its physical and chemical properties, a gold Au catalyst is frequently used.

But in order to incorporate these nanostructures into microelectronic devices, the nanowire growth process has to be fully compatible with the standard integrated circuit techniques. Aluminum is a standard metal in silicon process lines and the methods of deposition are well known. If aluminum could be used as the metal catalyst particle, the recent advances in nanowire growth could be exploited in microelectronics. However, using aluminum as a catalyst for VLS-assisted synthesis of silicon nanowire is not straightforward. The problems associated with using aluminum nanoparticles to catalyze nanowire growth are described in this paper.

II. THE VLS GROWTH MECHANISM

A. *VLS- assisted silicon nanowire growth*

The VLS mechanism can be divided into three main stages: nucleation (Figure 1a), precipitation (Figure 1b) and deposition (Figure 1c).

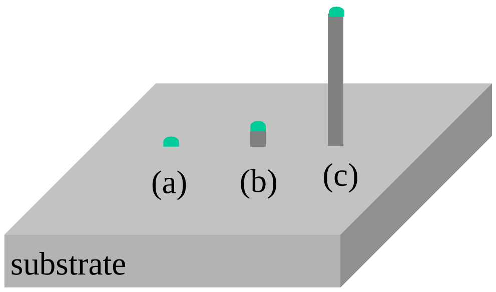

Figure 1: Main stages of VLS crystal growth (a) nanosized catalyst (b) precipitation (c) one-dimensional crystal growth

In the nucleation stage, nanosized metallic particles are formed on a substrate (Figure 2a). These particles can either be formed by laser ablation or by annealing a very thin metallic film above the eutectic temperature in order to break it into discrete islands. The diameter of the islands thus obtained is typically around 10-20 nm.

Then the source material carrier gas, generally silane SiH_4 or tetrachlorosilane $SiCl_4$ in the case of silicon nanowire growth, is introduced into a chamber maintained above the eutectic temperature (Figure 2b). The background pressure is used to control the catalyst size, and the temperature of the tube has to be adjusted in order to maintain the catalyst in the liquid state.

Table 1 shows the main alloys used in the synthesis of semiconducting nanowires assisted by VLS technique and the growth temperature.

Alloys	Eutectic temperature (bulk material)
Au-Si	360 ºC
Au-GaAs	630 ºC
Au-Ge	360 ºC
Ag-Si	837 ºC
Fe-Si	>1200 ºC
Al-Si	577 ºC
Al-Ge	419 ºC

Table 1: Eutectic temperatures of common alloys

The carrier gas reacts in the chamber to form liquid eutectic particles.

$$SiH_4 \xrightarrow{catalyst,H_2} metal\,catalyst - Si(l) + 2H_2(g)$$

$$SiCl_4 \xrightarrow{catalyst,H_2} metal\,catalyst - Si(l) + 2\,HCl(g)$$

Then the silicon diffuses through the catalyst droplets (Figure 2c). When the eutectic alloy becomes saturated, silicon precipitates at the liquid-solid interface; this is the precipitation (Figure 2d). This site is important because it will be a preferred site for further deposition of silicon. The sticking coefficient is higher on liquid than solid surfaces so consequently the crystal growth occurs only where the liquid metallic catalyst is present. In order to grow nanowires exactly where we need them, studies are currently proceeding to learn how to control the position of the catalyst nanodroplets.

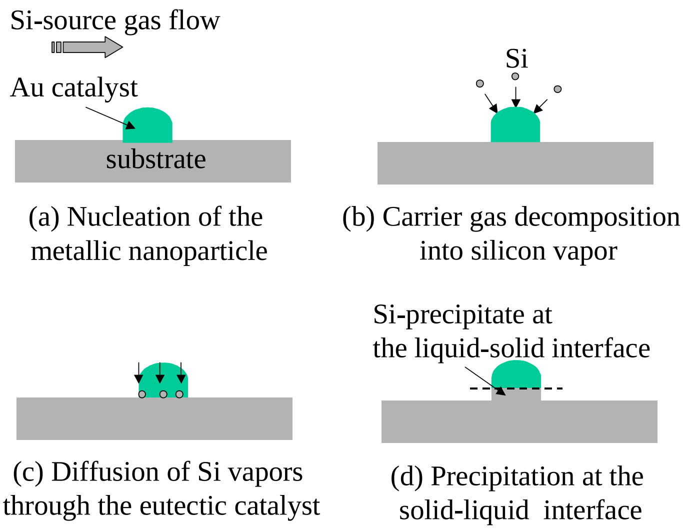

Figure 2: VLS-assisted growth of silicon nanowire

Anisotropic growth goes on while the gas flow is maintained; this step is the elongation or the growth itself (Figure 3).

At the end of the process, silicon nanowires of high purity are obtained except at one tip, which contains the solidified metallic catalyst. Moreover, a thin layer of native oxide often covers the whole structure. This is mainly due to air ambient native oxidation or remnants of oxygen in the tube.

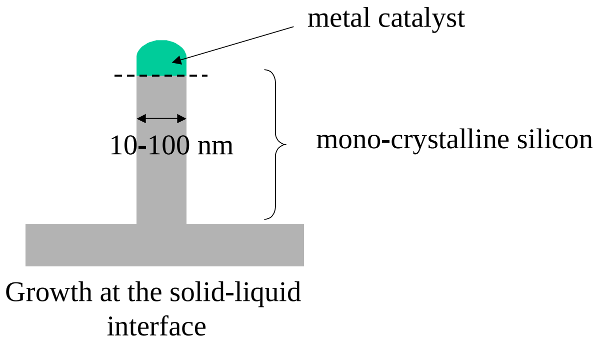

Figure 3: Silicon nanowire structure obtained by VLS synthesis

B. *The role of the metal catalyst*

The metal nanoparticle has a major role in vapor-liquid-solid assisted nanowire growth. The metal particle plays the act of the catalyst and determines the diameter of the nanostructures. Consequently, the choice of the metal, based on its physical and chemical properties, determines many of the nanowire properties. To be processed via the VLS growth mechanism, the metal has to be physically active, but chemically stable. To find an eligible metal, the phase diagram is first consulted to choose a material that forms a liquid alloy with the nanowire material of interest.

The phase diagram is also helpful for estimating the optimal composition and temperature for nanowire growth. Figure 4 shows a binary phase diagram of alloy suitable for VLS assisted growth of nanowires.

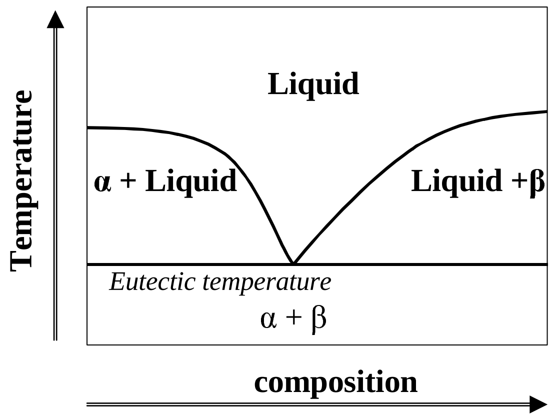

Figure 4: Binary phase diagram of alloy suitable for VLS mechanism

In the vapor-liquid-solid process, the Gibbs-Thomson equation places a lower limit on the wire diameters that can be achieved under a given set of conditions.

E. I. Givargizov studied also in detail the VLS crystal growth technique[13] in 1975. His study shows the equilibrium state is given by the equation in the case of silicon nanowire growth:

$$\Delta\mu_{nanowire} = \Delta\mu_{bulk} - 4\frac{\Omega\alpha}{d}$$

$$\Delta\mu_{bulk} = \mu_{bulk} - \mu_{vapor}$$

$$\text{and}\quad \Delta\mu_{nanowire} = \mu_{nanowire} - \mu_{vapor}$$

where $\mu_{nanowire}$, μ_{bulk}, and μ_{vapor} are the effective chemical potentials of silicon in the nanowire, in the bulk material and in the vapor phase respectively, d is the diameter of the nanowire, Ω is the atomic volume of silicon, and α the specific surface free energy of the wire.

This relation shows that there is a critical diameter, d_c, at which the growth stops completely and given by the following expression:

$$\frac{\Delta\mu_{bulk}}{kT} = \frac{4\Omega\alpha}{kT}\frac{1}{d_c}$$

where k is Boltzmann's constant and T the temperature, d_c the critical diameter.

This can be explained by the fact that for very small nanodroplets the effective chemical potential of silicon in the wire becomes higher than for the vapor phase.

Indeed, if the diameter of the catalyst is too small, the effective difference between the chemical potentials of silicon in the wire becomes more negative and the effective chemical potential in the vapor phase becomes higher, and the solubility of silicon becomes higher. Consequently, the saturation decreases. For most of the common alloys, the minimum critical radius of the liquid droplet is around a few hundred nanometers. That means nanowires with small enough diameter to present interesting nanosized-induced properties are not expected to grow under equilibrium conditions.

III. ALUMINUM AS A CATALYST

The use of aluminum as a catalyst for the silicon nanowire growth seems promising. Thermodynamically, aluminum is compatible with the VLS assisted silicon nanowire growth. Indeed, the phase diagram of the Al-Si alloy[14] has an eutectic reaction at 577 °C and an eutectic composition of 12.6 w% Si (Figure 5). As aluminum and silicon solidify in different structures, respectively faced centered cubic (FCC) and diamond cubic, two solid phases, called α and β are produced. At high temperature, the hypoeutectic alloy forms a rich aluminum α-phase solid. The hypereutectic alloy forms almost pure β phase silicon. Very little silicon dissolves in the α -phase and very little aluminum dissolves in the β-phase.

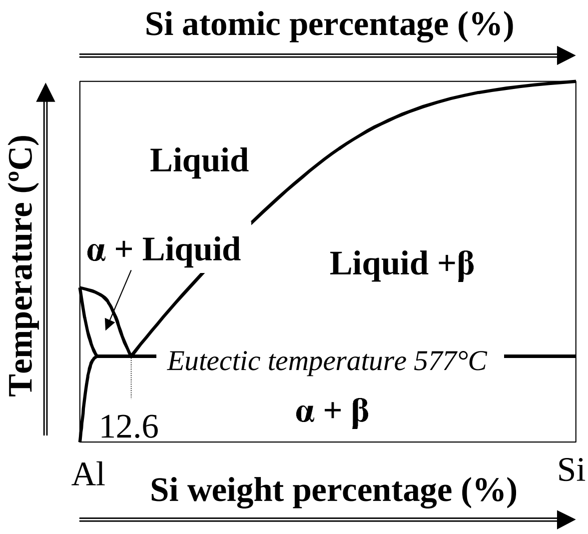

Figure 5: Binary phase diagram of Al-Si alloy

The Al-Si binary phase diagram is similar to that of Au-Si. (Figure 6). The eutectic composition is obtained at 577°C, which is much higher than in the Au-Si system.

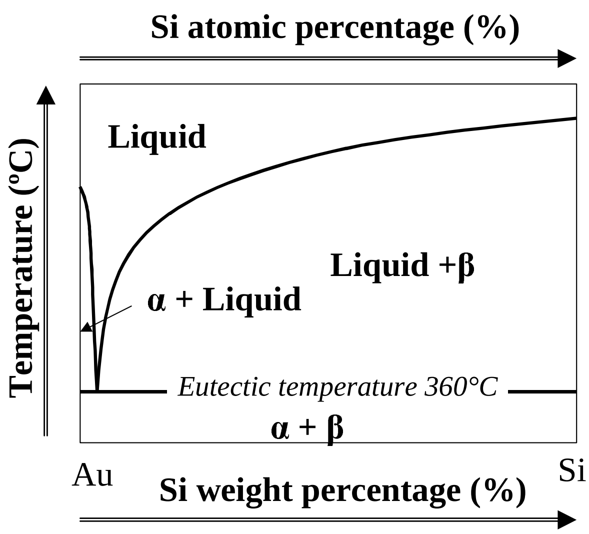

Figure 6: Binary phase diagram of Au-Si alloy

But even if thermodynamics allows the formation of catalyst nanodroplets above the eutectic temperature, the use of aluminum is complicated by another issue. Contrary to gold, which is chemically stable, aluminum is reactive in the ambient air. Aluminum can be easily oxidized to form aluminum oxide Al_2O_3. Aluminum oxide is a strong material that is extremely hard to reduce. All the more so because the incorporation of silicon nanowires is not compatible with a high thermal anneal which can modified dramatically the doping profiles. The aluminum native oxide is around 2-5 nanometers thick. The presence of aluminum oxide, which is not taken into account in the analysis of the binary phase diagram, disturbs the VLS crystal mechanism by preventing the diffusion of silicon vapor through the eutectic alloy. This layer is a diffusion barrier for silicon atoms.

We are currently investigating a technique to avoid the oxidation of aluminum after the nanocluster formation by heat treatment.

IV. CONCLUSION

Aluminum is an interesting alternative in order to incorporate nanowires in the front-end of a silicon IC process. The analysis of the Al-Si alloy binary phase diagram shows using such a catalyst is thermodynamically compatible with in a VLS-assisted one-dimensional synthesis. Nevertheless, compared to well-known nanowire growth assisted by gold catalyst, using aluminum involves using higher temperatures and dealing with the oxidation of aluminum. Thus far, no suitable conditions have been found for growth of aluminum catalyzed VLS silicon nanowires.

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