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# Growth Of Metal-Mediated Si Nanowires By LPCVD

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## Abstract

Silicon nanowires (NW) were grown on Si substrates via a Vapour-Liquid-Solid mechanism by Low-Pressure Chemical Vapour Deposition (LPCVD) from a disilane source. The influence of the growth parameters such as metal amount, operating pressure and substrate temperature and preparation on the Si NW morphology and structure has been investigated by SEM and XPS.

**Keywords:** Nanowires, silicon, CVD

## 1 Introduction

Nanotubes and nanowires are attracting increasing interest due to their physical properties and due to their vast range of possible applications as nanodevices [1,2]. Semiconductor nanowires can be used as building blocks for the fabrication of new photonic and electronic nanodevices and sensors [3,4]. In particular, silicon nanowires (SiNW) have the advantage of an easy integration into the existing silicon device technology together with the reproducible control of their electronic properties. Silicon nanowires have been recently used as highly sensitive sensors for biological and chemical species [5].

The study of the growth mechanism of Si wires has been started in the 60's and it is generally referred to as Vapour-Liquid-Solid (VLS) growth [6]. The VLS growth scheme requires the presence of a metal mediating the nanowire growth. At the growth temperature, a liquid alloy droplet containing the metal and Si is formed. The silicon diffuses preferentially into the liquid alloy and bonds to the Si at the liquid-solid interface resulting in the growth of a wire with the liquid alloy droplet on the top. A recent work by Schubert at al. [7] showed that SiNW VLS growth is influenced not only by the silicon in the gas phase but also by the Si adatoms diffusion on the surface of the whiskers.

Gold is commonly used as the nucleation- inducing metal [4,8-10] although the use of Fe [11,12] and other metals [13] or no catalyst at all [14] have been reported in the literature. The initial size of the catalyzing metal is crucial to determine the final diameter of the NW, as it was demonstrated for Au nanoclusters [15].

It is important to note that Au and Fe catalysts have liquid eutectic temperatures with Si below the growth temperatures used and hence SiNW formation is well described by the VLS scheme. On the other hand, Ti-induced nucleation of SiNW has been reported [16] at a growth temperature far lower than the lowest Ti-Si eutectic temperature. Therefore, it seems that also other mechanisms can lead to SiNW formation.

The most used method for growing SiNW is Chemical Vapour Deposition (CVD) from $SiH_4$. Among other techniques, SiNW formation by Pulsed Laser Deposition (PLD) [11,17] Gas-phase Molecular Beam Epitaxy (GS-MBE) [7] and physical deposition [12] has also been reported in the literature.

In this work we report about the synthesis of SiNW by means of Low- Pressure Chemical Vapour Deposition (LPCVD) using disilane ($Si_2H_6$) as the source gas. The SiNW synthesis was mediated by Au metal evaporation. The steps of SiNW films preparation were studied by X-Ray Photoelectron Spectroscopy (XPS) and the film morphology by Scanning Electron Microsocopy (SEM).

## 2 Experimental

Two types of substrates were used: clean crystalline Si(100) p-type B-doped wafers and amorphous Si substrates. The Si(100) wafer was cleaned by sputtering and annealing cycles in a 2 x $10^{-10}$ mbar base pressure Ultra High Vacuum (UHV) system. The UHV system consists of a deposition and an analysis chamber connected together by a sample transfer system. The analysis chamber is equipped with a MgK$\alpha$ (1253.6eV) X-Ray source, a double-pass CMA operating in retarding mode and LEED optics.

a-Si substrates of about 300nm thickness were deposited by CVD growth from disilane at 535ºC and 1.2mbar partial pressure on a native oxide covered Si(100) wafer substrate. The c-Si and a-Si surfaces were checked routinely by XPS. Temperatures were measured by a calibrated infrared pyrometer.

Au was deposited on the substrate by evaporation from a Mo crucible. The Au amount on the surface was calibrated by measuring by XPS the intensities $I_0$ and $I_1$ of the Si 2p core level before and after Au deposition, respectively, according to $I_1/I_0=e-(d/\lambda_{Au})$

where $\lambda_{Au}$ is the Au mean free path at about 1200eV kinetic energy which was set to 20Å and d is the Au layer average thickness, as at low coverages Au is known to form islands on the Si surface [18].

## 3 Results and discussion

Fig.1 shows the evolution of the Si2p and Au 4f core-levels XPS spectra after a 3Å Au deposition on a clean Si(100) and subsequent annealing at 500ºC for 60'. Upon Au deposition, a core-level shift occurs. The Si 2p shows a shift of about 0.2 eV towards lower binding energy (BE) in accord with the literature [19,20]. The Au 4f core-levels show a shift to higher BE by about 0.8eV indicating the formation of a Si-Au alloy [19,20]. Both peaks remain unshifted upon annealing up to 500ºC. Peak fitting analysis (not shown) of the $Au4f_{7/2}$ core-level has shown the presence of a small Au-metal component. On the

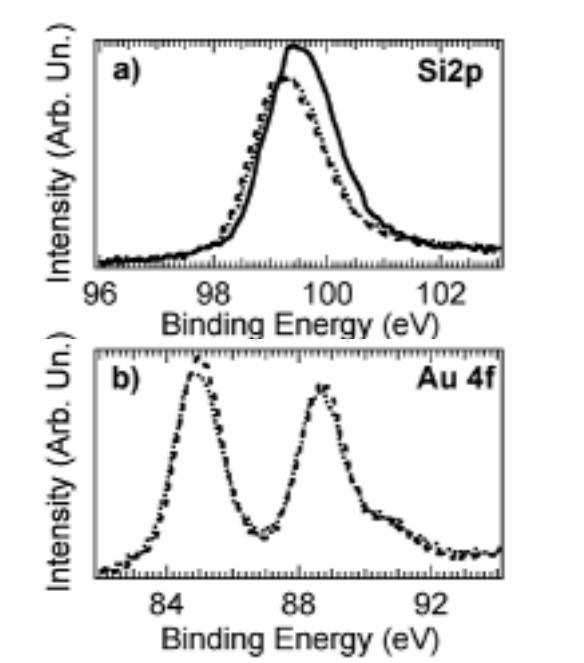


*Fig1. a) Si2p core-levels. b) Au4f core-levels Continuous line: clean Si(100); dots: after 3Å Au evaporation; dot-dashed lines: after 60' annealing at 500ºC*

other hand, no clear Si-Au component could be detected in the Si2p core-level. These results indicate that the sample surface after Au deposition up to 3Å consists of a reacted Au-Si layer on top of a Au metal layer with the bulk Si underneath. This picture agrees with the data reported in the literature for the Si(111) surface [20]. Further, annealing up to 500ºC does not lead to a fully reacted Au-Si overlayer. Fig. 2 shows an example of Si NW grown at 545ºC and 0.6mbar $Si_2H_6$ partial pressure on a Si(100) surface covered with 2Å Au without further annealing. The NW have about 150nm diameter and can be several microns long. Although most are bent, they do not exhibit kinks.

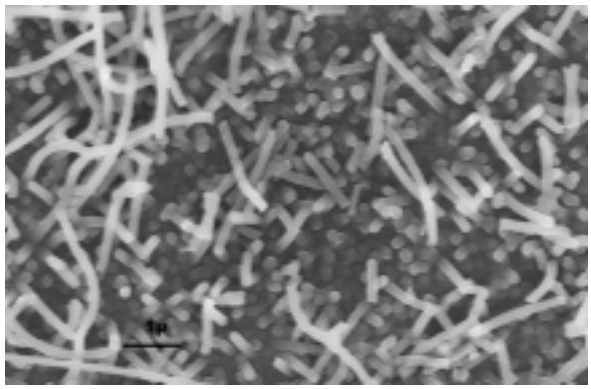

*Fig.2. SEM Micrograph of SiNW on Si(100)*

Fig.3 shows Si NW grown at 545ºC and 0.6mbar $Si_2H_6$ partial pressure on a Si(100) surface covered with 3Å Au and subsequent annealing at 500ºC. The ≈80nm diameter NW are tens of microns long and show bendings and curves among several straight sections.
Fig.4 shows that the NW seem to grow along a preferred direction with respect to the Si(100) substrate which could be tentatively guessed to be the {111} directions in agreement with previous results [8]. Figs. 5a and 5b show the XPS spectra of the Si 2p and Au4f core levels, respectively measured after 300nm a-Si deposition on a native Si(100) substrate,

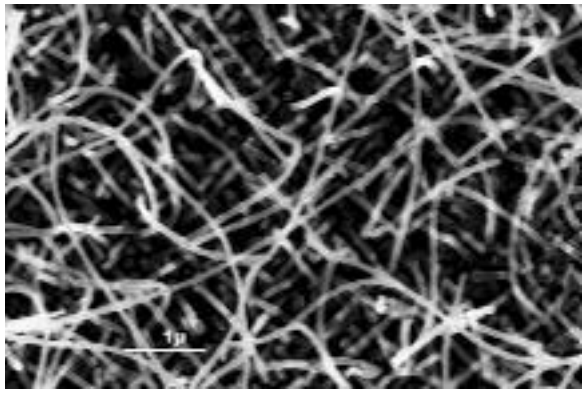

*Fig.3. SEM Micrograph of SiNW on Si(100). Substrate was annealed at 500ºC.*

2Å Au deposition and subsequent annealing at 590ºC for 120'. Similarly to the crystalline surface, the Si 2p peak shows a band bending shift of about 0.2eV to lower BE upon Au deposition. After annealing at 590ºC, the Si 2p peak maximum shows a clear 0.3eV shift to higher BE hinting to the formation of silicide [19,20].

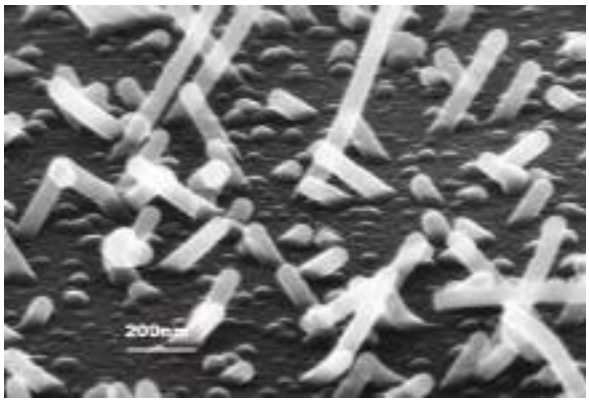


*Fig.4. SEM detail of SiNW on Si(100). Substrate was annealed at 500ºC*

The Au4f core-levels are shifted by 0.8eV to higher BE pointing to the formation of a Si-Au compound. The Au 4f peak energy position remains unchanged upon annealing at 590ºC and a significative intensity decrease is observed pointing to the disappearance of the Au metal layer and to Au diffusion into the bulk. It is worth noting that XPS data (not shown) taken on this type of substrate annealed at 482ºC are similar to those obtained on the annealed c-Si surface shown in

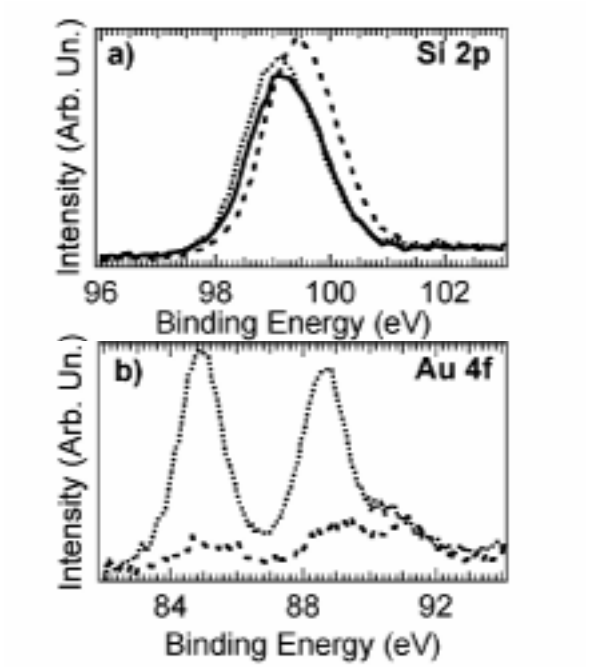


*Fig5. a) Si2p core-levels. b) Au4f core-levels Continuous line: a-Si layer; dots: after 2Å Au evaporation; dot-dashed lines: after 120' annealing at 590ºC*

Fig1. Fig.6 shows the morphology of Si NW grown at 515ºC and 0.6mbar $Si_2H_6$ partial pressure on an a-Si layer covered with 2Å Au and subsequent annealing at 590ºC. Due to the lower growth temperature, the NW show defects and a higher density of kinks. The NW diameter is ≈200nm. That can be related to the higher annealing temperature which causes the formation of larger islands on the surface.

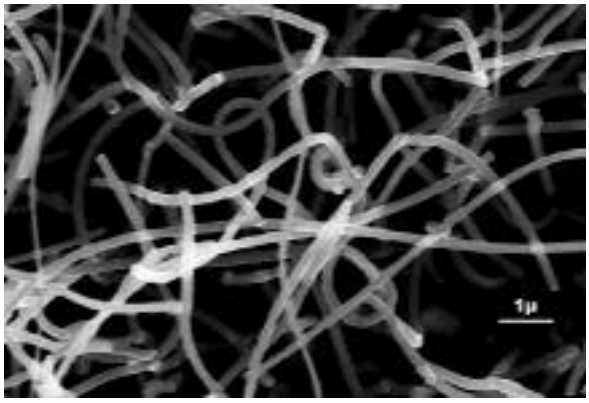


*Fig.6. SEM Micrograph of SiNW on a-Si. Substrate was annealed at 590ºC*

Differently from the crystalline Si(100) surface, the CVD growth at 545ºC and 0.6mbar $Si_2H_6$ partial pressure on an 1Å Au-covered a-Si substrate annealed up to 482ºC did not lead to the formation of SiNW.

## 4 Conclusions

In summary, Si NW were grown by CVD from $Si_2H_6$ using clean Si(100) and a-Si as starting substrates. In order to mediate the Si NW growth, Au metal was evaporated on the surfaces which were subsequently annealed up to 590ºC. The substrate structure and composition was monitored by XPS. Various NW morphologies depending on substrate and growth parameters have been observed by SEM. NW formation occurs on ordered Au-covered Si(100) surfaces indipendently from annealing. For a-Si substrates, NW growth requires annealing at temperatures higher than 482ºC.

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