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# Growth of Au-catalysed Si nanowires by low pressure chemical vapour deposition on Si(100) and amorphous Si surfaces

**A Santoni[1], F Jimenez Villacorta[2], A Rufoloni and A Mancini**

ENEA C.R. Frascati, v. E. Fermi 45, I-00044 Frascati, Italy

E-mail: santoni@frascati.enea.it

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**Abstract**

Au-mediated Si nanowires (SiNW) have been grown at low temperatures (500–560 °C) on crystalline Si(100) and amorphous Si surfaces by means of low pressure chemical vapour deposition from $Si_2H_6$ in the 0.05–1.2 mbar range. The influence of the substrates on the nanowire (NW) growth and morphology has been investigated by means of x-ray photoelectron spectroscopy and scanning electron microscopy. No NW growth has been observed on the Au covered amorphous Si surfaces. On both substrates, the NW exhibit inhomogeneous sidewalls and a new morphology showing NW entrenchment which has been explained as a consequence of vapour–liquid–solid growth termination due to Au diffusion on the SiNW sidewalls.

## 1. Introduction

The vast range of possible applications in nanodevices and their peculiar physical properties have drawn increasing attention to nanotubes and nanowires (NW) [1, 2]. Recent results have shown that these can be employed as building blocks for the fabrication of new photonic and electronic nanodevices and sensors [3, 4]. Among several different types of nanostructure, silicon nanowire (SiNW) systems have the advantage of easy integration into the existing silicon device technology. Moreover, 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 was started in the 1960s and this mechanism 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 and of a precursor gas. At the growth temperature, a liquid alloy droplet containing the metal and Si is formed. The silicon from the gas phase diffuses preferentially into the liquid alloy and bonds at the liquid–solid interface resulting in the growth of a wire with the liquid alloy droplet on the top. Recent work by Schubert *et al* [7] showed that SiNW

[1] Author to whom any correspondence should be addressed.
[2] Permanent address: ICMM-CSIC, Cantoblanco 28049-Madrid, Spain.

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VLS growth is influenced not only by the silicon in the gas phase but also by the Si adatom 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] and no catalyst at all [14] have been reported in the literature. Au and Fe catalysts have liquid eutectic temperatures with Si below the commonly used growth temperatures and hence SiNW formation is well described by the VLS scheme.

The most used method for growing SiNW is chemical vapour deposition (CVD) from $SiH_4$ or from $Si_2H_6$. At substrate temperatures above 430 °C the original precursor molecule is not particularly important for the structures forming on Si [15]. Among other techniques, SiNW formation by pulsed laser deposition (PLD) [11, 16], gas-phase molecular beam epitaxy (GS-MBE) [7] and physical deposition [12] have also been reported in the literature.

In this work, we report on the synthesis of SiNW by means of low pressure chemical vapour deposition (LPCVD) using disilane ($Si_2H_6$) as the source gas. Low pressure CVD at low temperatures allows better control and monitoring of the NW growth mechanism without inducing changes in the starting substrate. The SiNW synthesis was mediated by Au metal evaporation. In order to have a good control on the substrate initial composition and on the growth products, the steps of the SiNW film preparation were carried out in high vacuum (low pressure $10^{-8}$ mbar) and were studied using x-ray photoelectron spectroscopy (XPS) in a clean ultrahigh vacuum environment. Subsequently, the film morphology was investigated by *ex situ* scanning electron microscopy (SEM).

## 2. Experimental details

Two types of substrate were used: clean crystalline Si(100) p-type B-doped 0.7 Ω cm wafers and amorphous Si (a-Si) substrates. The Si(100) wafer was cleaned to show the $(2 \times 1)$ reconstruction by sputtering and annealing cycles in a $2 \times 10^{-10}$ mbar base-pressure ultrahigh vacuum (UHV) chamber. The growth system consists of an analysis chamber ($2 \times 10^{-10}$ mbar base pressure) and a deposition chamber (base pressure $<1 \times 10^{-8}$ mbar) connected together by a sample transfer system. The analysis chamber is equipped with a Mg K$\alpha$ (1253.6 eV) x-ray source, a double-pass CMA operating in retarding mode and LEED optics. The energy scale was calibrated by photoemission from a clean Au foil.

a-Si substrates of about 300 nm thickness were deposited by CVD from disilane at about 535 °C and 1.2 mbar partial pressure on a native oxide covered Si(100) wafer substrate. The c-Si and a-Si surfaces were checked routinely by XPS. The samples were resistively heated and growth temperatures in the range 500–560 °C were measured by a calibrated infrared pyrometer. The nanowires were grown by using disilane ($Si_2H_6$) as the precursor gas at partial pressures ranging from 1.2 to 0.05 mbar.

Au was deposited on the substrate by evaporation. 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 1200 eV kinetic energy which was set to 20 Å and $d$ is the Au layer average thickness, as at low coverages Au is known to form islands on the Si surface [17]. The error affecting this procedure is estimated to be about ±20%. The average thicknesses used were 15, 5, and 3 Å. SEM analysis (not shown) of clean Si(100) surfaces covered with about 3 Å of Au showed a uniform distribution of islands with diameters ranging from about 10 to 40 nm.

## 3. Results and discussion

Figure 1 shows the evolution of the Si 2p (figure 1(a)) and Au 4f core level XPS spectra (figure 1(b)) after a 3 Å Au deposition on a clean Si(100) wafer. Upon Au deposition, core level

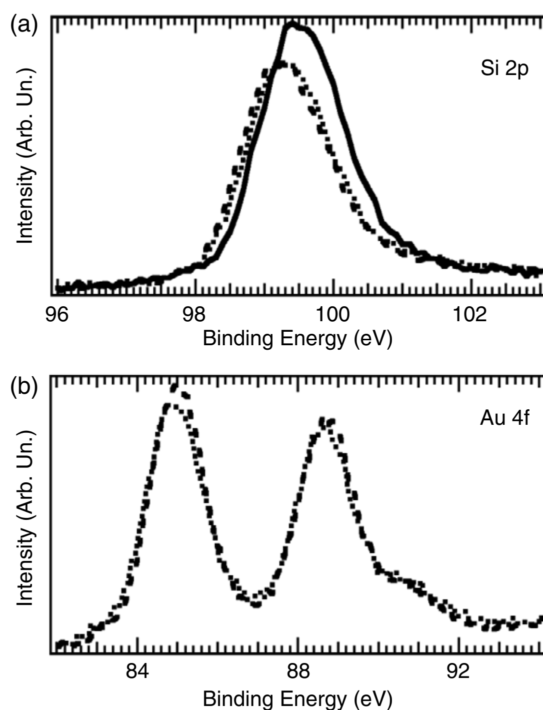


**Figure 1.** (a) Si 2p XPS core levels. (b) Au 4f XPS core levels. Continuous line: clean Si(100); dots: after 3 Å Au evaporation; dashed lines: after 60 min annealing at 500 °C.

shifts are observed. The Si 2p shows a shift of about $0.2 \pm 0.1$ eV towards lower binding energy (BE) due to band bending in accord with the literature [18, 19]. The Au 4f core levels show a shift to higher BE by about $0.8 \pm 0.1$ eV indicating the formation of a Si–Au alloy [18, 19]. The corresponding Au–Si (silicide) shift of the Si 2p level, expected at about 0.3 eV on the higher BE side [18, 19], is not observed. Peak fitting analysis of the Si 2p core level did not show the presence of a clear Si–Au component. On the other hand, the best fit of the background-subtracted Au $4f_{7/2}$ core level indicated the presence of a small metallic Au component. These results show that the sample surface after Au deposition up to 3 Å consists of a reacted Au–Si layer on top of a Au metal layer with the bulk Si underneath. Further, annealing up to 500 °C does not lead to a fully reacted Au–Si overlayer. This result obtained for the Si(100) surface is similar to the data reported in the literature for the Au/Si(111) surface [19].

Figure 2 shows an example of Si NW grown at 520 °C and 0.6 mbar $Si_2H_6$ partial pressure on a Si(100) surface covered with 3 Å Au and with subsequent annealing at 500 °C. The ≈80 nm diameter NW appear entangled, are tens of microns long and show bends and kinks among several straight sections. According to the literature [6, 8, 9], we observed that the NW diameter is strongly influenced by the metallic island dimensions (i.e. average thickness) and growth temperature. The partial pressure and deposition time (and again temperature) were observed to influence the NW length and geometry (i.e. defects). We have observed that also the growth time influences the NW diameter, i.e. samples grown with the same conditions but different times show thicker NW. That could be due to effects related to Au presence on the NW sidewalls as addressed in [7] and observed by TEM in [20] or, more generally, due to Au diffusion as recently demonstrated in [21]. Figure 3 shows that the SiNW can be connected

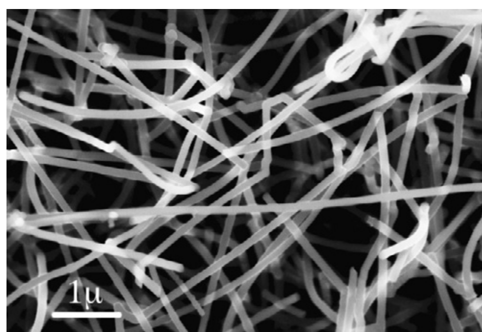


**Figure 2.** SEM micrograph of SiNW grown by LPCVD from $Si_2H_6$ on clean Si(100).

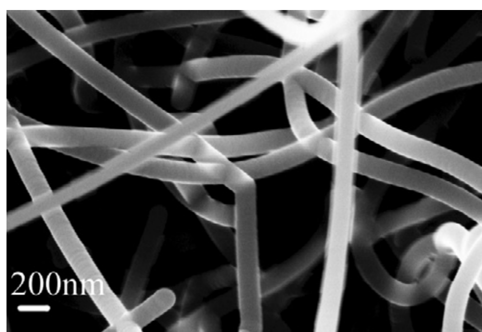


**Figure 3.** SEM micrograph showing 'lateral growth' on SiNW on Si(100). For an explanation see the text.

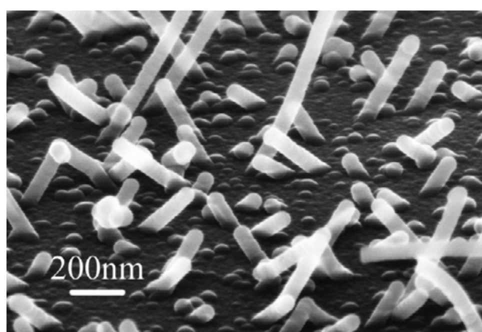


**Figure 4.** SEM detail of SiNW growing on Si(100) along preferred directions. For a discussion see the text.

laterally on the sidewalls. Such a 'lateral growth' could also be due to the presence of metal on the SiNW sidewalls as will be discussed in more detail below. Figure 4 shows that the SiNW seem to grow along a preferred direction with respect to the Si(100) substrate which could be qualitatively estimated from the angles formed with the (100) surface to be predominantly the {111} direction in agreement with previous results [3, 8, 11, 22].

Figures 5(a) and (b) show the XPS spectra of the Si 2p and Au 4f core levels, respectively, measured after 300 nm a-Si deposition on a native Si(100) substrate, subsequent 3 Å Au

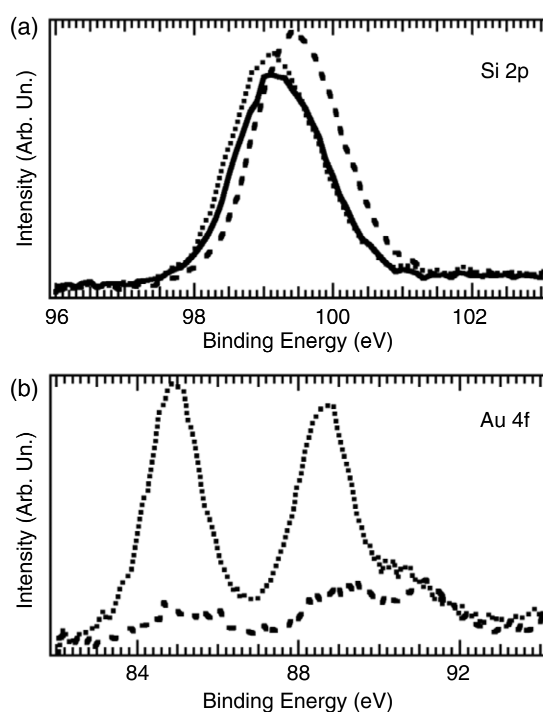


**Figure 5.** (a) Si 2p XPS core levels. (b) Au 4f XPS core levels. Continuous line: a-Si layer; dots: after 2 Å Au evaporation; dashed lines: after 120 min annealing at 590 °C.

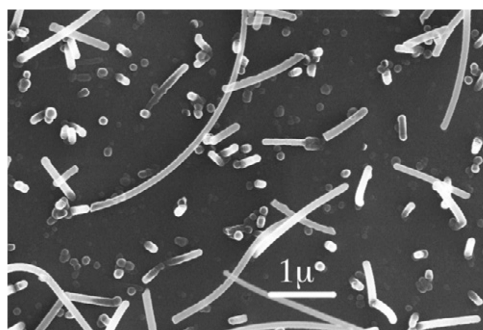


**Figure 6.** SEM micrograph of SiNW grown on a-Si at 534 °C and 0.05 mbar $Si_2H_6$ partial pressure.

deposition and final annealing at 590 °C for 120 min. Similarly to the crystalline surface case, the Si 2p peak shows a $0.2 \pm 0.1$ eV band bending shift to lower BE upon Au deposition. Correspondingly, the Au 4f core levels are shifted by $0.9 \pm 0.1$ eV to higher BE pointing to the formation of a Si–Au compound. After annealing at 590 °C for 120 min, the Si 2p peak maximum clearly shifts by $0.3 \pm 0.1$ eV to higher BE hinting at the formation of a thick silicide layer [18, 19]. The Au 4f peak energy position remains unchanged upon annealing at 590 °C for 120 min and a significant intensity decrease is observed pointing to Au diffusion into the bulk. XPS Si 2p and Au 4f data taken for non-annealed Au/a-Si surfaces (figure 5, dotted lines) are similar to those measured for the Au/Si(100) surface shown in figure 1. Therefore,

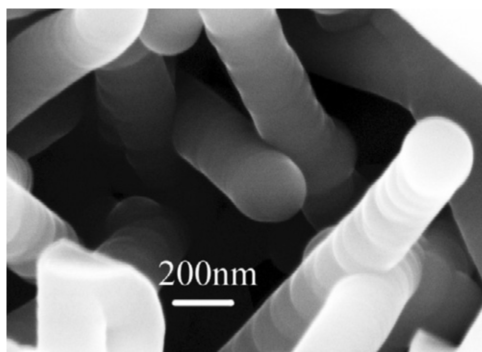


**Figure 7.** SEM micrograph showing SiNW exhibiting rippled sidewalls and a morphology due to CVD direct growth (see the text).

XPS for Au/a-Si with no annealing points to the presence of a three-layer structure. However, no nanowire growth has been detected on Au covered a-Si surfaces annealed below 590 °C for 120 min. As on the ordered Au/Si(100) surface nanowires are observed to grow without annealing, the absence of NW growth on a-Si surfaces annealed below 590 °C indicates that the presence of crystalline seeds is required for producing nanowires. The observed Au migration into deeper layers does not hinder the NW growth.

Figure 6 shows an example of Si NW grown at 534 °C and 0.05 mbar $Si_2H_6$ partial pressure on an a-Si layer covered with 3 Å Au and with subsequent annealing at 595 °C for 120 min. On the annealed a-Si surface the NW growth was observed to be influenced by the growth parameters in a way similar to the c-Si surface case. 'Lateral growth' is observed as well. On both c-Si and annealed a-Si surfaces the nanowires have been observed to exhibit rippled sidewalls as shown in figure 7. The periodicity and shape of the ripples in our SiNW appear in the SEM not homogeneous. The observed ripples appear different from the nearly equally spaced row of knots and necks reported in [23, 24] and referred to as 'periodic instability'. As reported in the literature, the origin of the ripples could be also due to formation of facets. Sawtooth faceting has been recently observed on Si NW by Ross *et al* [25]. According to their work, faceting may appear in any VLS growth where no stable orientations parallel to the growth direction exist. Figure 7 shows SiNW which have grown so close to each other as to show a sort of interpenetration. We believe that this peculiar interpenetration could be due to direct CVD growth on the NW sidewalls. According to recent results of Hannon and co-workers [21] on SiNW Au-mediated growth on Si(111) under clean growth conditions, Au diffusion from one NW to another along the NW sidewalls and on the surface in between has been demonstrated to control the length, shape and sidewall properties of the SiNW. In particular, results in [21] show that VLS growth stops when the Au in the droplet on the NW tip is consumed. This is the scenario causing the observed NW morphology in figure 7. VLS growth has stopped and direct CVD growth has taken over on the Au covered SiNW sidewalls causing the deposition of Si on the faceted VLS-grown nanowires which results in an increase of the NW diameter. If two or more NW are very close to each other, subsequent direct CVD growth causes an entrenchment of the NW as is visible in figure 7. On this view, the observed 'lateral growth' shown in figure 3 can be explained as well as the result of the embedding by direct CVD growth of two SiNW nearly touching each other. This picture is further supported by XPS data taken for these samples after NW growth which did not show any Au on the surface, thus confirming CVD Si deposition.

## 4. Summary

SiNW were grown by CVD from $Si_2H_6$ on clean Si(100) and a-Si substrates using evaporated Au metal to mediate the SiNW growth. The substrate structure and composition were monitored by XPS. SiNW formation was observed to occur on ordered Au covered Si(100) surfaces independently of annealing. For a-Si substrates, NW growth requires annealing at temperatures higher than 595 °C for 120 min. Various NW morphologies depending on substrate and growth parameters have been observed by SEM. The SiNW show preferential growth directions and exhibit inhomogeneous sidewalls. Furthermore, lateral branches and a peculiar entrenchment between SiNW have also been observed, which have both been explained as due to CVD direct growth occurring after termination of VLS growth caused by Au diffusion.

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