Experimental evidence of the generation of gaseous SiO as precursor for the growth of SiO_x nanowires

A. Gomez-Martinez^a, F. Marquez^b, and C. Morant^{a*}

^a Departamento de Fisica Aplicada and Instituto Nicolas Cabrera, Universidad Autonoma de Madrid, E-28049 Madrid, Spain

^b Nanomaterials Research Group, School of Natural Sciences and Technology, University of Turabo, Gurabo, PR 00778, USA

* Corresponding author. Tel.: +34 91 4974924

E-mail address: c.morant@uam.es

Abstract

The Vapor-Liquid-Solid process is a fundamental and widely used mechanism for the growth of nanowires. In this article, experimental observations have been carried out to explain the growth mechanism of silicon-based nanowires using a solid-bulk silicon source as unique precursor. The synthesis consisted of a thermal treatment at 900 °C under an Ar-H₂ atmosphere with a low residual O₂ concentration. The presence of SiO in gaseous phase, originated via the active oxidation of the Si substrate, is shown as the principal factor responsible for the nanowires growth, via a process commonly termed as Solid-Vapor-Liquid-Solid.

Keywords: SiO_x nanowires; Active oxidation; VLS process; CVD; SiO gas

1. Introduction

The vapor-liquid-solid (VLS) mechanism has been one of the most accepted and employed methods for the growth of 1-D silicon nanostructures during the last decades. This mechanism, firstly described by Wagner and Ellis [1] in 1964, proved to be a new procedure for the growth of crystal whiskers from vapor precursors by the use of a metal impurity. The role of the impurity is to provide a preferential site for the supersaturation, nucleation, and subsequent growth of the nanowires from the gaseous species involved in the process. The mechanism was named “VLS” because of the three phases involved.

This mechanism has been widely studied and the process seems to be clear when a silicon gaseous precursor is used (SiCl₄, SiH₄). A thermodynamic description of the process was formulated by Wacaser et al. [2], proposing a preferential interface nucleation model for the growth of the nanowires. Afterwards, an extensive kinetic analysis, based on this assumption, was developed by Shakthivel et al. [3].

Currently, several efforts have been made in order to avoid the use of unsafe and highly flammable vapor-phase silicon precursors like silane (SiH₄), using instead a solid source. Nanowires grown under these conditions, using solid precursors, normally exhibit an amorphous structure with nonstoichiometric amounts of oxygen. The explanation seems to reside in the mechanism by which silicon atoms moves from the solid bulk to the metal catalyst liquid droplet. Yan et al. [4] and Yu et al. [5] described the process as a pure diffusion mechanism, justifying the amorphous state of the

nanowires by the fast speed of the growth. Accordingly, this mechanism of growth was termed as Solid-Liquid-Solid (SLS). However, latter reports of Bahloul-Hourlier et al [6], Hourlier et al [7] and Lee et al. [8] declined this possibility, having found no evidence of a driving force that thermodynamically explains the growth of the nanowires. They postulated, instead, the necessary existence of a gaseous SiO phase as precursor for the nanowires. The SiO vapor would be released from the interface between bulk silicon and its native oxide, via the reaction $\text{Si(s)} + \text{SiO}_2\text{(s)} \rightarrow 2\text{SiO(g)}$. This mechanism commonly is termed as a Solid-Vapor-Liquid-Solid (SVLS) process.

Recently, a series of papers have been reported by Shalav, Kim and Elliman [9 - 12] in which they develop a complete and detailed model explaining the growth of sub-stoichiometric silica nanowires via the active oxidation of Si substrates. Several thermodynamic and kinetic experiments [13, 14] performed under ultrahigh vacuum (UHV) conditions have shown that at low oxygen pressures and high substrate temperature, the Si surface can be rapidly etched by the O_2 while producing SiO vapor, via the active oxidation reaction $2\text{Si(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{SiO(g)}$ [15 - 17].

The present work aims to provide some light on the process of nanowires growth via a series of experimental evidences where some of the subjects discussed above have been tested. These subjects include the question about the existence or not of a gaseous SiO precursor, its origin and whether a diffusion mechanism is required. Understanding the growth mechanism of the nanowires becomes a crucial issue on the way towards a further refinement of the process, whose optimization might allow the implementation of this material on future commercial applications.

2. Materials and methods

Silicon oxide nanowires (SiO_x NWs) were synthesized via an annealing process in a tubular quartz furnace at atmospheric pressure. The thermal treatment consists of a ramp-up rate of $25\text{ }^\circ\text{C/min}$ to a final temperature of $900\text{ }^\circ\text{C}$, followed by one hour plateau, all while flowing a mixture of H_2 (99.9992 %) and Ar (99.9992 %) in a proportion of 3:1 in volume; and finally a cooling ramp rate of $20\text{ }^\circ\text{C/min}$ in Ar atmosphere (flow rate of 600 ml/min). The process is summarized in Fig. 1.

Fig.1 Diagram of the thermal treatment performed for the nanowires synthesis.

Two different substrates were used for the SiO_x NWs growth: Si <100> wafers (300 μm thickness, p-type, single-side polished) and 304 stainless steel foils (1.3 mm thickness).

A Dual Ion Beam Sputtering deposition system was used for the pre-treatment of both substrates. An accelerating voltage of 250 V was applied in the Kaufman-type ion source used to sputter a TiN target (99.5 % pure, Kurt J. Lesker Inc.) and a SiO target (99.9 % pure, Cerac Inc.), respectively. The deposition time for the TiN film was of 30 min, obtaining a thickness of 120 nm, as measured by a quartz balance. The deposition time and thickness for the SiO₂ film were 40 min and 600 nm, respectively.

A Sputter Quorum (Q150T-S) system was used for evaporating 10 nm thick gold films employed as catalyst during the process of synthesis.

After the SiO_x NWs synthesis, the morphology of the samples was analyzed by Field-Emission Scanning Electron Microscopy (FE-SEM, Philips XL30 S-FEG) and High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM 3000F). The chemical composition was analyzed with Energy Dispersive X-ray Spectroscopy (EDX, OXFORD INCA) integrated in the HRTEM system. The nanowires were detached from the substrates surface by ultrasonication in ethanol and deposited on a standard copper grid for the analysis with HRTEM. Transversal sections of the samples were prepared by mechanical cleavage.

3. Results and discussion

3.1 Evidences of a gaseous phase

It has been shown that membranes are an adequate way to generate nanoparticle patterns from a thin layer of catalytic material [18, 19]. Similar effect could be obtained by using a sufficiently thin porous film, which enables the diffusion of the catalytic metal through it. In this work, a thin film coverage of TiN was deposited on Si substrates in order to get two goals simultaneously. By one hand, it is possible to obtain a porous film due to fact that the TiN grows in a columnar structure that maintains good properties of porosity below a certain thickness [20]. On the other hand, the obtained film presents a good elastic and hard behavior due to the mechanical properties of the TiN [21, 22], maintained even at high temperatures.

With this aim, the surface of a Si wafer was coated by a 120 nm-thick TiN layer. On the top of this layer, a thinner Au layer was deposited in order to create catalytic centers through the TiN layer, which acts as a mask. Details of the process are summarized in Fig. 2.

Fig. 2 Schematic representation of the SiO_x NWs growth process from a silicon substrate coated with a TiN layer, as prepared (a) and the sequential steps under the thermal treatment (b,c,d), as labelled.

During the first stage of the thermal treatment, the gold layer is decomposed into droplets (Fig. 2b). Then a diffusion process takes place in which gold crosses the porous TiN layer and the Si native oxide layer, until reaching the Si substrate (Fig. 2c). At that time and close to the synthesis temperature of 900 °C, two parallel processes occur (Fig. 2d). On the one hand, Au in contact with the Si substrate, at a temperature higher than the Au-Si eutectic temperature (363 °C) forms an Au-Si alloy. On the other hand, silicon exposed to the H₂-Ar atmosphere (with 1-2 ppm of O₂ impurities, according to distributor specifications) gives way to a new gaseous-phase species. In a first approach, it could be provided by the reaction between the Si of the wafer and the native SiO₂ layer via:

However, although this possibility was not discarded, FE-SEM cross-section images of the samples after SiO_x NWs synthesis revealed the generation of etched-voids (Fig. 3). This suggests that once the layer of native oxide (only a few nanometers thick) is exhausted, silicon keeps on being consumed. An active oxidation of the substrate, as had been reported by Shalav, Kim and Elliman [9 - 11] is consistent with this process. By this reaction, silicon atoms combined with the residual oxygen of the atmosphere produce a gaseous SiO phase [15 - 17] via:

The SiO gas, generated through (I) and mainly (II), is incorporated on the Au-Si nucleation centers in order to form the nanowires. Simultaneously, an etched-void is generated underneath, as shown in Fig. 3a.

Fig. 3: FE-SEM cross-section images of the SiO_x NWs grown from the Si-TiN interface. Silicon is consumed in the process as evidence the etch-voids underneath the nanowires, a) and b). Bubbles trapped in the coating, c) and d), prove the existence of a gaseous species.

An enlarged image at the bottom of the nanowire (Fig. 3b) clearly shows how the nucleation is originated in several sites against the coating TiN layer. At each of these nucleation centers, a VLS mechanism takes place, continuing to spread upwards across the layer (which occasionally deforms or even breaks the coating) to join on the surface as a single nanowire. In other words, nanowires grow vertically attached to the TiN coating like a “tree from the roots”.

Furthermore, the 120 nm thickness of the TiN layer makes it ductile enough to store possible gas species formed during annealing. Figs 3c and 3d show evidences of a gaseous expansion from inside to outside the coating layer at the time of the growth, in the Si-TiN interface, while silicon from the substrate is consumed.

These results clearly demonstrate the presence of a gaseous species, which results in either, nucleation and subsequent growth of the SiO_x nanowires or expansion of the upper TiN layer, generating bubbles.

3.2 Silicon as necessary reactant

In order to demonstrate the need of a pure Si source in the process, acting as primary reactant, a new experiment was performed using SiO_2 nanospheres deposited on a stainless steel, as substrate. A silicon fragment positioned over the spheres was used as unique silicon supply. From now on, this silicon fragment will be referred as *Si-hat* to shortening.

Silica nanospheres (SNs) were synthesized by the hydrolysis of tetraethyl orthosilicate in ethanol as reported in literature [23]. Details of the procedure, as well as the validity of employing these structures for the production of nanowires, have been previously

reported [24]. Stainless steel samples, covered by the SNs and coated with 10 nm Au layer, placed according to the scheme of Fig. 4, were annealing following the process depicted in Fig. 1.

Sample configuration

Fig. 4: Schematic representation of the sample as prepared and FE-SEM images of the substrate, after the SiO_x NWs synthesis, at different distances from the Si-hat: several millimeters away a), few micrometers b), at the edge c), and over d) the Si-hat.

FE-SEM images of Fig. 4 show sections of the sample at different distance from the Si-hat, after the SiO_x NWs synthesis. On the region furthest away from the Si-hat (several millimeters of distance) the Au film has decomposed into droplets on the top of the SNs surface but there was no nanowires growth, as shown in Fig. 4a. In contrast, the nanowires started to growth at few micrometers away from the Si-hat (Fig. 4b) and became longer on the region close to its edge (Fig. 4c). Finally, Fig. 4d shows a huge amount of SiO_x NWs synthesized just below the Si-hat, which grow from the catalytic metal droplets, covering entirely the spheres.

This experiment clearly shows that the precursor of the SiO_x NWs growth comes from the Si-hat, since there were no nanowires on the region situated further from it. In addition, a progressive evolution of the nanowires length was observed by reducing the distance to the Si hat. Consequently, it is also clear that the only presence of the SiO_2 nanospheres is insufficient to promote the growth of the SiO_x NWs; being required a primary silicon source for the synthesis.

3.3 Transport mechanism of the precursor

In view of the results, which support the need of an initial silicon source in the process, the remaining uncertainty was to understand the mechanism involved in the transport of silicon atoms from the source to the gold nanoparticles. A new experiment was designed in order to provide a homogeneous medium, in which the SiO_2 spheres were changed by a continuous layer of SiO_2 that covered completely the Si substrate. Moreover, with the aim of avoid a superficial diffusion of the silicon-based precursor, the Si-hat, previously coated with a 10 nm thick film, was placed over the sample **some millimeters** elevated by two pieces of mica, as is depicted in the scheme of Fig. 5.

Stainless steel samples, covered with a 600 nm-thick SiO_2 layer and a 10 nm Au coating were annealing following the process for the synthesis of SiO_x NWs described in Fig. 1. The results of the synthesis are illustrated in the FE-SEM images of Fig. 5. The sample, placed face to face with the *Si-hat*, exhibited the presence of nanowires homogeneously distributed across the entire surface. A characteristic picture of this growth is shown in Fig 5a. Meanwhile, FE-SEM image of Fig 5b show how the *Si-hat* was harshly etched by the effect of gold.

Significantly, it has been noted that the presence of Au enhances the process of active oxidation on silicon, in the way that the bare silicon wafer under the same thermal treatment hardly suffer any etching (not shown here).

Fig. 5: Schematic representation of the sample as prepared and FE-SEM images of the substrate a), and the *Si-hat* b) after the synthesis process.

The observation of the growth of nanowires in these conditions is irrefutable proof that a diffusion process does not take place; as the necessary condition, which is direct contact between the two surfaces is not met in this case. However, gas phase transport of reactants SiO is consistent with this behavior.

Fig. 6: TEM image of the synthesized nanowires a), zoomed HR-TEM image in the middle of the nanowire b) and its corresponding in-situ EDX analysis c).

In order to avoid any possible doubt about the nature of the nanowires, these were detached from the substrate to analyze them by HR-TEM. Fig. 6a shows a TEM image of some of these nanowires and Figs 6b and 6c show, respectively, the zoomed HR-

TEM image taken at half-length of the nanowire and the corresponding EDX analysis carried out at this point. The analysis confirmed that the predominant element in the composition of the nanowires was silicon with small amounts of oxygen, obtaining, as result, a sub-stoichiometric silicon dioxide. Furthermore, the HR-TEM image revealed that these SiO_x NWs ($x < 2$) exhibited a homogeneous amorphous structure.

4. Conclusions

The responsible mechanism of the SiO_x NWs growth has been studied through a series of experimental results. These nanowires were synthesized via thermal treatment at 900 °C at atmospheric pressure and under low O_2 concentration atmosphere, using a Si <100> wafer as unique silicon source. After the experiments, the following conclusions can be summarized:

- The generation of a gaseous species became apparent by observing the bubbles generated in the Si-TiN interface at the time of the SiO_x NWs growth. As well as the cavities beneath the nanowires indicated that silicon had been consumed during the process.
- The need of a primary silicon reactive was verified, since SiO_2 nanospheres by themselves, without the presence of the *Si-hat*, did not produce any nanowires growth. Noting further that the nanowires length was increased by reducing the distance to the Si hat.
- Surface diffusion was discarded as the main transport mechanism of the growth, since SiO_x NWs were synthesized even when the silicon source (*Si-hat*) and the substrate were not in direct contact during the synthesis.

In summary, all the experimental observations in this work are a clear proof of the existence of a vapor-phase SiO coming from the active oxidation of the Si substrate; which unequivocally confirms that the growth of the SiO_x NWs ($x < 2$) is leaded by a gas phase transport process, according with the proposal of a SVLS mechanism.

Acknowledgments

The authors gratefully recognize the financial support provided by the MICINN of Spain through the grant MAT2010-19804 and by the US DoE, through the Massie Chair project at University of Turabo. A. Gomez-Martinez wishes to acknowledge a FPI fellowship from the Autonomous University of Madrid and the Spanish Ministry of Education and Science.

References:

- [1] R. S. Wagner, and W. C. Ellis, The Vapor-Liquid-Solid Mechanism of Crystal Growth and Its Application to Silicon, Trans. Metall. Soc. AIME. 233 (1965) 1053-1064
- [2] B. A. Wacaser, K. A. Dick, J. Johansson, M. T. Borgstrom, K. Deppert, and L. Samuelson, Preferential Interface Nucleation: An Expansion of the VLS Growth Mechanism for Nanowires. Adv. Mater. 21 (2009) 153-165
- [3] D. Shakthivel, and S. Raghavan, Vapor-liquid-solid growth of Si nanowires: A kinetic analysis. J. Appl. Phys. 112 (2012) 1-14

- [4] H. F. Yan, Y. J. Xing, Q. L. Hang, D. P. Yu, Y. P. Wang, J. Xu, Z. H. Xi, and S. Q. Feng, Growth of amorphous silicon nanowires via a solid-liquid-solid mechanism. *Chem. Phys. Lett.* 323 (2000) 224-228
- [5] D. P. Yu, Y. J. Xing, Q. L. Hang, H. F. Yan, J. Xu, Z. H. Xi, and S. Q. Feng, Controlled growth of oriented amorphous silicon nanowires via a solid-liquid-solid (SLS) mechanism. *Physica E*. 9 (2001) 305-309
- [6] D. Bahloul-Hourlier, and P. Perrot, Thermodynamics of the Au-Si-O system: Application to the synthesis and growth of silicon-silicon dioxide nanowires. *J. Phase Equilib. Diffus.* 28 (2007) 150-157
- [7] D. Hourlier, P. Lefebvre-Legry, and P. Perrot, Preparation of silicon-based nanowires and the thermochemistry of the process. XXXV Jeep - 35th Conference on Phase Equilibria. 2 (2009) 1-4
- [8] J. H. Lee, M. A. Carpenter, and R. E. Geer, Novel growth mode of solid-liquid-solid (SLS) silica nanowires. *J. Mater. Res.* 26 (2011) 2232-2239
- [9] T. H. Kim, A. Shalav, and R. G. Elliman, Active-oxidation of Si as the source of vapor-phase reactants in the growth of SiO_x nanowires on Si. *J. Appl. Phys.* 108 (2010) 1-3
- [10] A. Shalav, T. Kim, and R. G. Elliman, SiO_x Nanowires Grown via the Active Oxidation of Silicon. *IEEE J. Select. Topics Quantum Electron.* 17 (2011) 785-793
- [11] Y. Yang, A. Shalav, T. Kim, and R. G. Elliman, The effect of annealing temperature, residual O₂ partial pressure, and ambient flow rate on the growth of SiO_x (x) nanowires. *Appl. Phys. A*. 107 (2012) 885-890
- [12] R. G. Elliman, T. H. Kim, A. Shalav, and N. H. Fletcher, Controlled Lateral Growth of Silica Nanowires and Coaxial Nanowire Heterostructures. *J. Phys. Chem. C*. 116 (2012) 3329-3333
- [13] F. W. Smith, and G. Ghidini, Reaction of Oxygen with Si(111) and (100): Critical Condition for the Growth of SiO₂. *J. Electrochem. Soc.* 129 (1982) 1300-1306
- [14] D. Starodub, E. P. Gusev, E. Garfunkel, and T. Gustafsson, Silicon oxide decomposition and desorption during the thermal oxidation of silicon. *Surf. Rev. Lett.* 6 (1999) 45-52
- [15] T. Engel The interaction of molecular and atomic oxygen with Si(100) and Si(111). *Surf. Sci. Rep.* 18 (1993) 91-144
- [16] J. R. Engstrom, D. J. Bonser, M. M. Nelson, and T. Engel, The reaction of atomic oxygen with Si(100) and Si(111) I. Oxide decomposition, active oxidation and the transition to passive oxidation . *Surf. Sci.* 256 (1991) 317-343
- [17] I. Kinefuchi, H. Yamaguchi, Y. Sakiyama, S. Takagi, and Y. Matsumoto, Inhomogeneous decomposition of ultrathin oxide films on Si(100): Application of Avrami kinetics to thermal desorption spectra. *J. Chem. Phys.* 128 (2008) 1-6
- [18] K. K. Lew, and J. M. Redwing, Growth characteristics of silicon nanowires synthesized by vapor-liquid-solid growth in nanoporous alumina templates. *J. Cryst. Growth.* 254 (2003) 14-22
- [19] F. Marquez, C. Morant, V. Lopez, F. Zamora, T. Campo, and E. Elizalde, An alternative route for the synthesis of silicon nanowires via porous anodic alumina masks. *Nanoscale Res. Lett.* 6 (2011) 1-7

- [20] Y. M. Chen, G. P. Yu, and J. H. Huang, On the porosity of TiN films deposited by HCD ion plating. *Surf. Coat. Technol.* 155 (2002) 239-244
- [21] Z. Liqiang, Y. Huisheng, P. Xiaolu, G. Kewei, and A. A. Volinsky, Microstructure, residual stress, and fracture of sputtered TiN films. *Surf. Coat. Technol.* 224 (2013) 120-5
- [22] C. Morant, S. Garcia-Manyes, F. Sanz, J. M. Sanz, and E. Elizalde, Nanotribological properties of CN/TiCN/TiN/Si multilayer as determined by AFM. *Nanotechnology.* 16 (2005) 11-17
- [23] W. Stober, A. Fink, and E. Bohn, Controlled Growth of Monodisperse Silica Spheres in the Micron Size. *J. Colloid Interface Sci.* 26 (1968) 62-69
- [24] A. Gomez-Martinez, F. Marquez, E. Elizalde, and C. Morant, Microspheres for the Growth of Silicon Nanowires via Vapor-Liquid-Solid Mechanism. *J Nanomater.* (2014) 1-8