Published in final edited form as:

Nanotechnology. 2010 November 19; 21(46): 465604. doi:10.1088/0957-4484/21/46/465604.

Scalable flame synthesis of SiO₂ nanowires: dynamics of growth

Antonio Tricoli^{1,3}, Marco Righettoni¹, Frank Krumeich¹, Wendelin J Stark², and Sotiris E Pratsinis¹

¹Particle Technology Laboratory, Department of Process and Mechanical Engineering, Institute of Process Engineering, ETH Zurich, 8092 Zurich, Switzerland ²Department of Chemistry and Applied Biosciences, Functional Materials Laboratory, ETH Zurich, 8092 Zurich, Switzerland

Abstract

Silica nanowire arrays were grown directly onto plain glass substrates by scalable flame spray pyrolysis of organometallic solutions (hexamethyldisiloxane or tetraethyl orthosilicate). The silicon dioxide films consisted of a network of interwoven nanowires from a few to several hundred nanometres long (depending on the process conditions) and about 20 nm in diameter, as determined by scanning electron microscopy. These films were formed rapidly (within 10–20 s) at high growth rates (ca 11–30 nm s⁻¹) by chemical vapour deposition (surface growth) at ambient conditions on the glass substrate as determined by thermophoretic sampling of the flame aerosol and microscopy. In contrast, on high purity quartz nearly no nanowires were grown while on steel substrates porous SiO₂ films were formed. Functionalization with perfluorooctyl triethoxysilane converted the nanowire surface from super-hydrophilic to hydrophobic. Additionally, their hermetic coating by thin carbon layers was demonstrated also revealing their potential as substrates for synthesis of other functional 1D composite structures. This approach is a significant step towards large scale synthesis of SiO₂ nanowires facilitating their utilization in several applications.

1. Introduction

Nanowires have numerous potential applications as flexible [1] and integrated [2] circuits, plasmonic waveguides [3], super-wetting membranes [4], gas sensors [5], and for energy generation [6] and storage [7]. Silica nanowires, in particular, can emit stable blue light over a hundred times brighter than that of porous silicon [8]. Their mechanical strength is two orders of magnitude larger than that of bulk silica and considerably higher than conventional high strength materials like steel and Kevlar [9]. Very recently, it was shown that films containing SiO₂ nanowires are super-hydrophilic and thus exhibit an anti-fogging functionality [10]. Commercial utilization of nanowires, however, has been hindered by the lack of technology for their large scale manufacture.

In contrast to nanoparticle commodities that are produced in several million tons per year by large scale flame reactors [11], nanowires are still produced in relatively small quantities by rather elaborate processes. For example, during vapour–liquid–solid (VLS) growth, a metal catalyst nanoparticle, deposited on the substrate surface, is required for the growth of each nanowire [12]. This allows an excellent control over wire diameter [13, 14], length [14], spacing and alignment [15], but increases production costs while limiting process scalability. Catalyst-free nanowire growth has been achieved by other approaches such as molecular

beam epitaxy [16], without offering, however, a more cost effective or scalable alternative to VLS. A further restriction to the scalability of nanowire synthesis methods is that for several applications, such as anti-fogging [10] and self-cleaning [17] surfaces, the nanowires should be well dispersed and anchored on the substrate surface. This is best achieved when nanowires are grown directly from the target surface. In fact, nanowire growth in the gas phase would most probably result in entangled structures similar to flame-made carbon nanotubes [18].

Recently, we have reported the spontaneous growth of SiO₂ nanowires by flame spray pyrolysis (FSP) [10]. For a narrow window of process parameters, SiO₂ nanowires nucleated on a glass substrate in cross flow to the flame aerosol (radicals and/or clusters) [10]. As a result, nanowire growth was obtained without catalyst nanoparticles or pre-treatment of the substrate surface. This approach is particularly attractive as flame technology has a proven scalability and undisputably high production rates [11]. Furthermore, although in FSP reactors the flame temperature reaches up to 2400 K [19], the substrate surface experiences only moderate temperatures and thus it is possible to rapidly coat also fragile or sensitive substrates (e.g. micro-hot plates) [20].

Here, we have investigated systematically the dynamics of flame synthesis of SiO₂ nanowires focusing on the key process parameters that determine the nanowire characteristics. The effects of substrate material, precursor concentration and composition on nanowire growth rate, spacing and morphology were assessed and a first mechanism is proposed for flame synthesis of SiO₂ nanowires. The feasibility of switching from super-hydrophilic to hydrophobic coatings by functionalization of the SiO₂ nanowire surface was demonstrated. Furthermore, encapsulation of such nanowires with carbon was achieved showing potential for the synthesis of other composite 1D nanostructures.

2. Experimental details

2.1. Flame spray synthesis of SiO₂ nanowires and surface functionalization

A FSP reactor was used in combination with a substrate holder (figure 1) for SiO₂ deposition onto steel, plain (VWR, ECN 631-1550) and quartz glass substrates [10]. Silica precursor solutions were fed to the FSP unit consisting of hexamethyldisiloxane (HMDSO, Aldrich, purity >99%) or tetraethyl orthosilicate (TEOS, Aldrich, purity >99%) diluted in xylene (Fluka, purity >98.5%) with a total metal (Si) concentration of 0.01–0.5 mol l⁻¹. This solution was supplied at a rate of 5 ml min⁻¹ through the FSP nozzle and dispersed to a fine spray with 5 l min⁻¹ oxygen (pressure drop 1.5 bar). That spray was ignited by a supporting ring-shaped premixed methane/oxygen flame (CH₄ = 1.5 l min⁻¹, O₂ = 3.2 l min⁻¹). An additional 5 l min⁻¹ sheath oxygen was supplied from an annulus surrounding that flame to assure excess oxidant flow. The temperature behind and in front of the substrate was measured by n-type thermocouples. During growth, the substrate was placed at 20 cm height above the burner (HAB) and its front temperature reached 550 ± 20 °C. After deposition, the films were mechanically stabilized by rapid *in situ* annealing [20] at moderate flame conditions [10]. Functionalization of the nanowire surface was obtained by impregnation with a solution of perfluorooctyl triethoxysilane (purity 97%) in hexafluorobenzene with a volumetric ratio of 1:8. Thereafter, the substrates were dried for 1 h in ambient air and then under vacuum for an additional 30 min.

2.2. Nanowire characterization

Transmission electron microscopy (TEM) was conducted in a Tecnai F30 (FEI; Eindhoven), operated at 300 kV. Scanning transmission electron microscopy (STEM) images were obtained with a high-angle annular dark field (HAADF) detector. The focused electron beam

was then set on the nanowires to analyse their composition by energy dispersive x-ray spectroscopy (EDXS; detector (EDAX) attached to the Tecnai F30 microscope). The morphology, patterning characteristics and thickness of the deposited films were investigated by SEM with a LEO 1530 Gemini (Zeiss/LEO, Oberkochen) and a Tecnai F30 microscope (FEI (Eindhoven); field emission cathode, operated at 300 kV). The average nanowire growth rate and spacing were determined by measuring and counting the nanowire length and number per surface on several spots. Before transferring the samples to the focused ion beam (FIB) column (Zeiss NVision 40), the sample was sputtered with a ca 10 nm thick Pt layer to improve the contrast. Thereafter, a hole was drilled through the sample by a Ga ion beam exposing the nanowire–substrate interface.

3. Results and discussion

3.1. Control of SiO₂ nanowire length and growth rates

Figure 1 shows a schematic of the nanowire synthesis process. A combustible liquid solution containing the SiO₂ precursor (hexamethyldisiloxane, HMDSO) was sprayed and ignited in a FSP reactor. The product aerosol was impinged on a plain glass substrate, placed at a selected height [10] above the burner. This led to spontaneous self-assembly and uniform growth of SiO₂ nanowires (figure 2(a)). The resulting nanowires (figures 2(b) and (c)) were mostly orthogonal to the substrate surface and had a homogeneous length (110–600 nm) with a rather uniform diameter of 20 nm and dense wire-to-wire spacing (ranging from 70 to 100 nm) that is comparable to state-of-the-art VLS growth [21]. The reproducibility of these properties was confirmed by SEM analysis of large areas of the substrate on numerous samples. To clarify the role of the Si precursor (HMDSO) against the possible nanowire growth solely from the substrate, these experiments were repeated by FSP of pure solvent (xylene). This resulted in no nanowire formation and thus confirmed the prevalent role of Si precursor in the nanowire synthesis process.

Table 1 summarizes the employed process parameters and resulting nanowire properties. To capture the initial growth dynamics, a low precursor concentration (0.01 M, HMDSO) was used, that resulted in an average nanowire growth rate of $11.5 \pm 2 \text{ nm s}^{-1}$. Figure 3(a) shows tilted SEM images of such films, after 10 s growth, consisting of ca 110 nm long SiO₂ nanowires. At high magnification (figure 3(b)), the nanowires had a constant diameter without any visible discontinuity or segregation in the proximity of their tip. These observations may eliminate the possibility of VLS-related growth that requires segregated catalytic particles usually visible on the nanowire tip [12]. However, a slight enlargement of the nanowire is observed at its interface with the substrate. This suggests a transition in the growth regime that could take place just after nucleation. Increasing the nanowire growth time from 10 to 20 s increased the length of the nanowires from ca 110 to 230 nm (figures 3(c) and (d)) without altering their diameter and spacing. This indicates that deposition on the nanowire wall and thus radial growth does not compete with axial growth.

Figure 4 shows the effect of precursor concentration on the resulting film morphology at constant growth time (10 s): increasing the precursor concentration from 0.01 ((a), (b)) to 0.05 M ((c), (d)) increased the average nanowire growth rate from 11.5 to 30 nm s⁻¹ without affecting nanowire morphology (diameter or spacing) as was observed also for the growth time (figure 3). These high growth rates result from the relatively high precursor molar flux ($2.5 \times 10^{-4} \text{ mol min}^{-1}$) supplied here. This is about an order of magnitude higher than that obtained by state-of-the-art metal-organic vapour phase epitaxy growth (MOVPE) [21]. As a result, the process time required here (seconds to minutes) by FSP synthesis of nanowires is significantly shorter than that (minutes to hours) by MOVPE [21], laser ablation [22] and other nanowire synthesis methods. At a higher precursor concentration of 0.5 M, a dendritic, lace-like morphology (figures 4(e) and (f)) was observed. The latter is, commonly, obtained

for FSP direct deposition of nanoparticles such as TiO_2 [10], SnO_2 [20, 23], $\text{SnO}_2\text{-SiO}_2$ [24], $\text{Eu:Y}_2\text{O}_3$ [25] and LiMn_2O_4 [26]. In fact, at the high precursor concentrations (0.1 M) commonly used for FSP synthesis of materials [27], nanoparticles nucleate homogeneously in the gas phase as has been confirmed by thermophoretic sampling for TiO_2 [10] and SnO_2 [28]. However, here, we show (figures 4(a)-(d)) that decreasing the precursor concentration below a minimal threshold (0.1 M) prevents formation of nanoparticles in the gas phase. This is attributed to the R-SiO_x vapour saturation ratio in the FSP aerosol being below the critical value for SiO_2 nucleation in the gas phase [10], where R is an organic functional group derived from the SiO_2 precursor. As it is discussed below, however, a low precursor concentration (e.g. 0.05 M) and thus inhibition of nanoparticle nucleation is not a sufficient condition for nucleation of the nanowires.

3.2. Effect of nanowire precursor and substrate composition

The nanowire nucleation mechanism was investigated further (figure 5) by varying the substrate and precursor compositions. Figures 5(a) and (b) show SEM images of quartz and steel substrates that were placed in the FSP aerosol (0.05 M, HMDSO) for 20 s as with the plain glass substrates above (figures 4(c) and (d)). Using quartz substrates (figure 5(a)) inhibited nanowire nucleation at all precursor (HMDSO) concentrations. In contrast, steel substrates promoted the formation of a continuous, porous SiO_2 thin film (figure 5(b)). On plain glass, impurities may act as catalysts for nanowire nucleation while on pure quartz glass no such impurities are available for nanowires to grow. In fact, analysis of the plain glass composition by EDXs revealed small traces of K, Zn and Ca. Isolation of these impurities on the plain glass surface and reaction with the Si-loaded FSP aerosol (radicals) could lead to nucleation of isolated SiO_x domains and successively to nanowire growth. In contrast, on steel substrates the whole metallic surface may act as a catalyst resulting in a continuous SiO_2 film.

Replacing the HMDSO by tetraethyl orthosilicate (TEOS) in a 0.05 M solution and FSP depositing for 20 s on plain glass substrate led also to nucleation of nanowires (figure 5(c)) with similar diameter and length, but wider spacing (190 ± 20 nm) than with HMDSO (100 ± 20 nm). This is partially attributed to the TEOS having half of the Si content present in the HMDSO molecules which halves the R-SiO_x concentration locally resulting in fewer nucleation events. The different reaction kinetics, however, of HMDSO and TEOS could also play a role in determining the nanowire nucleation rate.

3.3. Nanowire morphology, composition and applications

The nanowires (figures 6(a) and (b)) were amorphous with a rather constant diameter. At higher magnifications (figures 6(c) and (d)), two types of nanowire endings were visible: a rounded one (figure 6(c)) with a wider diameter and a planar one (figure 6(d)) with the same diameter as the wire body. Both endings were amorphous and their different shapes are attributed to one being the root and the other the tip of the nanowire. This rounded root is in agreement with the slight enlargement of the nanowire body observed in the proximity of the substrate surface (figures 3(b) and (d)).

The electron diffraction (ED) patterns (figure 6(e)) obtained from a large agglomerate (figure 6(a)) of these nanowires confirmed the presence of only amorphous material not showing any trace of crystal structure. This was in good agreement with the HR-TEM (figures 6(c), (d)) and EDXS analysis (figures 6(g) and (h)) of the nanowire compositions revealing the presence of only Si and O atoms that usually form amorphous SiO_2 in the highly oxidizing FSP environment [19]. This precludes a possible VLS synthesis mechanism, as a segregated, catalytic active tip is required to drive the nanowire growth [12]. Nanowire growth without the presence of a crystalline nanoparticle was also reported

for oxide assisted growth (OAG), a method able to produce a host of 1- and 2D nanostructures.

Figure 7 shows a schematic of a possible mechanism for flame aerosol nucleation and growth of SiO_2 nanowires. First a SiO_x cluster is anchored on the substrate by CVD on an impurity site, in agreement with the observed nucleation dynamics on metal, quartz and plain glass substrates (figures 3, 4, 5(a) and (b)). The non-bonded silicon atoms in the SiO_x cluster act as a reaction site for the impinging R- SiO_x from the flame aerosol resulting in, first, the isotropic (radial and axial) growth of the nanowire. This is in agreement with the enlargement of nanowire body near the substrate (figure 3) and the rounded endings (roots) observed upon their detachment from the substrate surface (figures 6(a) and (c)). The catalytic activity of SiO_x clusters has been confirmed also for oxide assisted growth (OAG) of Si nanowires [29]. However, here, in contrast to OAG [29], we have observed that nanowire growth can proceed also in strongly oxidative conditions (flame environment) leading to the formation of pure SiO_2 nanowires. Simultaneously, oxidation (SiO_x to SiO_2) of the nanowire wall passivates its surface preventing further reaction with the incoming R- SiO_x aerosol and radial nanowire growth. At steady state, equilibrium is reached between further SiO_x deposition and its oxidation resulting in a constant nanowire diameter, as observed by SEM (figure 3) and TEM (figure 6(b)).

A possible application of the present nanowire synthesis process is the deposition of films with controlled wetting properties [4]. We have recently shown that the large nanowire specific surface area in combination with the super-hydrophilic properties of flame-made SiO_2 surface leads to anti-fogging coatings [10]. Here, we demonstrate that functionalization of the SiO_2 surface with a super-hydrophobic group (e.g. by impregnation with a perfluorooctyl triethoxysilane solution) can be utilized for switching between super-hydrophilic (figure 8(b)) and hydrophobic (figure 8(c)) surfaces. In more detail, figure 8(a) shows the contact angle (θ) between a water droplet and an uncoated plain glass substrate. The contact angle remains above 25° even after 30 s. However, after coating the plain glass with SiO_2 nanowires, θ decreases below 8° (figure 8(b)) in less than 0.5 s contact time. This is attributed to the porosity of the coating and to the super-hydrophilicity of the flame-made SiO_2 nanowire surface [10]. As a result, water droplets cannot stabilize on the coated glass surface and thus an anti-fogging effect is achieved. In contrast, after functionalization with perfluorooctyl triethoxysilane, θ is increased to above 115° (figure 8(c)) showing the potential for preparation of super-hydrophobic surfaces. This is attributed to the reaction of the perfluorooctyl triethoxysilane with the SiO_2 nanowire surface that leads to its coating with hydrophobic groups.

A further application of the presented SiO_2 nanowire films is their utilization as templates for synthesis of one-dimensional arrays of other functional materials such as carbon [1]. Figure 9 shows that it is possible to hermetically coat the SiO_2 nanowire surface with carbon by standard sputtering methods. The SiO_2 core is still visible inside this nanocomposite and acts as a support for the carbon film. Such structured arrays of dielectric materials (e.g. SiO_2) and carbon have potential for the large scale fabrication of nanoscale memory and may offer an alternative to the utilization of more expensive carbon nanotubes [30]. In fact, the specific SiO_2 precursor yield over the substrate surface was of the order of $0.02\% \text{ cm}^{-2}$ resulting in a nanowire specific production rate of $0.4 \text{ mg m}^{-2} \text{ s}^{-1}$. The total production rate of the present system can be easily enhanced by increasing the substrate surface and the number of FSP nozzles as pressure controlled chambers and electrically heated ovens are not required.

4. Conclusions

In summary, we have demonstrated the synthesis of SiO₂ nanowires on plain glass substrates by flame spray pyrolysis of standard CVD Si precursors (e.g. HMDSO, TEOS) without any substrate pre-treatment or catalytic nanoparticles. This is an important step toward large scale synthesis of nanowires. We have determined that nanowire nucleation takes place below a maximal precursor concentration and requires the presence of active sites on the target substrate (e.g. impurities of plain glass). This resulted in the rapid coating of plain glass substrates with SiO₂ nanowires and in controlled wetting properties with potential for the rapid fabrication of super-wetting membranes [4] and self-cleaning surfaces (super-hydrophobic coatings) [17]. For example, hydrophobic surfaces were obtained by functionalization of the nanowire surface with a perfluorooctyl triethoxysilane solution. Furthermore, we have shown that these nanowires provided an excellent support for nanotemplate fabrication of one-dimensional arrays of other materials such as carbon and thus offer an alternative route for synthesis of composite materials.

Acknowledgments

Electron microscopy was performed at the Electron Microscopy ETH Zurich (EMEZ). We thank Karsten Kunze (EMEZ) for the FIB measurements and Michael Rossier (Functional Materials Laboratory ETH Zurich) for his assistance on surface functionalization. Support by the European Research Council and Swiss National Foundation (# 200021_130582/1) is greatly appreciated.

References

- [1]. McAlpine MC, Ahmad H, Wang DW, Heath JR. Nat. Mater. 2007; 6:379. [PubMed: 17450146]
- [2]. Ferry DK. Science. 2008; 319:579. [PubMed: 18239115]
- [3]. Pyayt AL, Wiley B, Xia YN, Chen A, Dalton L. Nat. Nanotechnol. 2008; 3:660. [PubMed: 18989331]
- [4]. Yuan JK, Liu XG, Akbulut O, Hu JQ, Suib SL, Kong J, Stellacci F. Nat. Nanotechnol. 2008; 3:332. [PubMed: 18654542]
- [5]. Arbiol J, Cirera A, Peiro F, Cornet A, Morante JR, Delgado JJ, Calvino JJ. Appl. Phys. Lett. 2002; 80:329.
- [6]. Wang ZL, Song JH. Science. 2006; 312:242. [PubMed: 16614215]
- [7]. Chan CK, Peng HL, Liu G, McIlwrath K, Zhang XF, Huggins RA, Cui Y. Nat. Nanotechnol. 2008; 3:31. [PubMed: 18654447]
- [8]. Yu DP, Hang QL, Ding Y, Zhang HZ, Bai ZG, Wang JJ, Zou YH, Qian W, Xiong GC, Feng SQ. Appl. Phys. Lett. 1998; 73:3076.
- [9]. Brambilla G, Payne DN. Nano Lett. 2009; 9:831. [PubMed: 19170550]
- [10]. Tricoli A, Righettoni M, Pratsinis SE. Langmuir. 2009; 25:12578. [PubMed: 19621912]
- [11]. Pratsinis SE. Prog. Energy Combust. Sci. 1998; 24:197.
- [12]. Wagner RS, Ellis WC. Appl. Phys. Lett. 1964; 4:89.
- [13]. Duan XF, Wang JF, Lieber CM. Appl. Phys. Lett. 2000; 76:1116.
- [14]. Duan XF, Lieber CM. Adv. Mater. 2000; 12:298.
- [15]. Yan C, Zhang T, Lee P. Appl. Phys. A. 2009; 94:763.
- [16]. Martin H, Anders G, Sonia C-B, Francesca P, Joan Ramon M, Abstreiter G, Jordi A, Lars S, Anna Fontcuberta i M. Nanotechnology. 2009; 20:075603. [PubMed: 19417424]
- [17]. Blossey R. Nat. Mater. 2003; 2:301. [PubMed: 12728235]
- [18]. Height MJ, Howard JB, Tester JW, Sande JBV. Carbon. 2004; 42:2295.
- [19]. Mädler L, Kammler HK, Mueller R, Pratsinis SE. J. Aerosol Sci. 2002; 33:369.
- [20]. Tricoli A, Graf M, Mayer F, Kühne S, Hierlemann A, Pratsinis SE. Adv. Mater. 2008; 20:3005.
- [21]. Borgstrom MT, Immink G, Ketelaars B, Algra R, Bakkers E. Nat. Nanotechnol. 2007; 2:541. [PubMed: 18654364]

- [22]. Shi WS, Zheng YF, Wang N, Lee CS, Lee ST. *Adv. Mater.* 2001; 13:591.
- [23]. Madler L, Roessler A, Pratsinis SE, Sahm T, Gurlo A, Barsan N, Weimar U. *Sensors Actuators B.* 2006; 114:283.
- [24]. Tricoli A, Graf M, Pratsinis SE. *Adv. Funct. Mater.* 2008; 18:1969.
- [25]. Kubrin R, Tricoli A, Camenzind A, Pratsinis SE, Bauhofer W. *Nanotechnology.* 2010; 21:225603. [PubMed: 20453290]
- [26]. Chew SY, et al. *J. Power Sources.* 2009; 189:449.
- [27]. Strobel R, Pratsinis SE. *J. Mater. Chem.* 2007; 17:4743.
- [28]. Keskinen H, Tricoli A, Marjamaki M, Makela JM, Pratsinis SE. *J. Appl. Phys.* 2009; 106:084316.
- [29]. Zhang RQ, Lifshitz Y, Lee ST. *Adv. Mater.* 2003; 15:635.
- [30]. Jang JE, Cha SN, Choi YJ, Kang DJ, Butler TP, Hasko DG, Jung JE, Kim JM, Amaratunga GAJ. *Nat. Nanotechnol.* 2008; 3:26. [PubMed: 18654446]

Figure 1.

Schematic of nanowire growth by flame spray pyrolysis (FSP). A combustible liquid Si precursor solution is sprayed and ignited at atmospheric pressure. The resulting aerosol (radicals and clusters) is impinged orthogonally on a glass substrate leading to spontaneous nucleation of SiO₂ nanowires on its surface. The nanowire length is controlled by the precursor concentration exposure (residence) time of the substrate to the flame aerosol.

Figure 2. SEM images of SiO₂ nanowires (a) spontaneously grown by FSP on plain glass substrates. Rapid (20 s) impingement of low concentration FSP aerosol (HMDSO, 0.01 M) leads to homogeneous self-assembly of nanowires with a diameter of ca 20 nm ((b), (c)) and dense wire-to-wire spacing (70–100 nm).

Figure 3.

SEM images of the early stage nanowire morphology (side view, tilted 45°) at a deposition time of 10 ((a), (b)) and 20 s ((c), (d)) for constant precursor (HMDSO) concentration (0.01 M) on plain glass substrates at two magnifications. Just after nucleation ((a), (b)), the nanowires grow nearly perpendicular to the substrate surface with a sharp diameter and length distribution. Increasing the deposition time to 20 s ((c), (d)) increased their length without altering their diameter and spacing.

Figure 4.

SEM images (side view, tilted 45°) of SiO₂ films obtained at different (HMDSO) precursor concentrations and constant deposition time (10 s) at two magnifications. Up to a concentration of 0.05 M ((a)–(d)), nanowires with homogeneous diameter and spacing are self-assembled on the substrate surface. Decreasing that concentration from 0.05 to 0.01 M decreases the nanowire growth rate from 30 to 11.5 nm s^{−1}. In contrast, at 0.5 M ((e), (f)) nanoparticles nucleate in the gas phase and subsequently are deposited on the substrate forming a porous (98%) film with a dendritic morphology.

Figure 5.

SEM images of SiO_2 deposited by FSP of precursor (HMDSO or TEOS) solutions on quartz glass (a), steel (b) and plain glass (c) substrates. On high purity quartz (a) nearly no nanowires are detected. In contrast, on steel substrates (b) the whole surface may catalyze the reaction with the FSP aerosol resulting in a porous SiO_2 film ((b), inset). In fact, defects present on the plain glass may allow nucleation and growth of SiO_2 nanowires on its entire surface. However, utilizing TEOS (c) as precursor, a larger nanowire spacing was achieved than that with HMDSO (figure 3).

Figure 6.

HR-TEM images ((a)–(d)), electron diffraction (ED) pattern (e), STEM (f) and EDXS ((g), (h)) analysis of SiO₂ nanowires (HMDSO at 0.05 M and $t_s = 20$ s) upon removal from the substrate. The nanowire body has a homogeneous diameter ((a), (b)) and two kinds of endings: a rounded one (c) and a nearly planar (d) one. Both endings are amorphous ((c), (d)) in agreement with the ED pattern of nanowires (e). In fact, they are made solely of Si and O atoms ((g), (h)), in contrast to VLS growth where a segregated tip drives the nanowire growth [12].

Figure 7.

Schematic of nanowire growth by FSP. First, a R-SiO_x group reacts with an impurity site on the substrate. Thereafter, incoming R-SiO_x vapour continues the (isotropic) growth in both radial and axial directions (rounded root). Oxidation of the active SiO_x surface to SiO₂ delimits further radial expansion while the active SiO_x tip catalyzes the reaction with the incoming FSP aerosol resulting in the growth of nanowires with constant diameter.

Figure 8.

Water droplets on an uncoated (a) glass substrate and with as-deposited (b) or functionalized (c) nanowires. It is demonstrated that by functionalization of the high surface area of the nanowire coatings, it is possible to switch between super-hydrophilic (b) and hydrophobic (c) coatings. The inset in (b) shows a magnified view of the as-deposited nanowires.

Figure 9.

TEM image of carbon-coated SiO₂ nanowires. Carbon sputtering of the nanowires on the plain glass substrate leads to rapid formation of hermetically coated nanowires. This demonstrates the potential for large scale nanotemplating of 1D nanostructures other than SiO₂ by the presented synthesis method.

Table 1

Summary of the utilized process parameters and resulting nanowire properties.

Concentration (mol l ⁻¹) ^a	Precursor	Substrate	Morphology	Growth rate (nm s ⁻¹) ^b	Spacing (nm)
0.01	HMDSO	Plain glass	Nanowires	11.5	70 ± 20
0.05	HMDSO	Plain glass	Nanowires	30	100 ± 20
0.5	HMDSO	Plain glass	Nanoparticles	—	—
0.05	HMDSO	Quartz glass	—	—	—
0.05	HMDSO	Steel	Porous film	—	—
0.05	TEOS	Plain glass	Nanowires	20	190 ± 20

^aConcentration in the liquid precursor.

^bAverage growth rate in the first 20 s.