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Fabrication of silica nano wires on the internal perimeter of narrow bore fused silicia tubing by non-isothermal etching

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An method for fabrication of long silica nano wires is presented. The nano structured material is an integral part of the inner surface of narrow bore fused silica capillary tubing. The wire preparation method is based on a hydrothermal action and decomposition of 2-chloro-1,1,2-trifluoroethyl methyl ether at elevated temperature. In our previous work, reproducible nano wire outgrowth could only be accomplished in capillaries with an inner diameter less than10 μm [1], and the centre of the capillary lumen remained free of wires. In the present article we report on nano wire outgrowth in capillaries with larger inner diameters. These wires are entangled via carbon nucleating particles and stretch across the entire lumen of the capillary. The long nano wire outgrowth was induced by a time dependent, non isothermal etching of the capillaries. Suggested mechanisms for the growth process are discussed.

1. Introduction

Nano-structured silica has a vast number of possible applications, e.g. in micro-electronics, micro fluidics, optics, micro sensors and actuators as well as in particle technology. Often, the methodology used in synthesizing nano-structured silica entities requires advanced instrumentation such as excimer laser ablation technology [2–4] or complex template assisted polymerizations/condensations [5–9]. Attempts have also been made to mimic biosilicification [10–12].

Both in separation science and micro fluidics, fused silica tubing has, since it first was presented in this context by Dandeneau *et al.* [13], come to play a very important role due to its purity, flexibility, optical, thermal and physicochemical properties. Fused silica tubing is currently the material of choice for capillary gas chromatography, capillary electrophoresis, as well as packed and open tubular liquid chromatography (both pressure- and electro osmotically driven). The nature of the silica surface has been thoroughly characterized in terms of chemical modifications [14–16], smoothness [17] and its electrostatic properties [18–20]. However, the possibilities to alter the morphology of the fused silica surface have only gained limited attention. Pesec *et al.* changed the surface morphology of fused silica capillaries by means of etching with ammonium hydrogen fluoride [21] and the modified capillaries were successfully used in electro-driven separations [21–23].

A study of the action of the thermal decomposition products of 2-chloro-1,1,2-trifluoroethyl methyl ether as agents in the fabrication of silica nano wires inside fused silica capillaries has recently been reported by our group [1]. The concept of using this particular chemistry stems from original work presented by Tesařik *et al.* [24] as well as Pretorius *et al.* who used the etching reagent and borosilicate or soda lime glasses as substrates [25, 26].

In the present paper, we report our second study on growing silica nano wires attached to the inner surface of fused silica capillary tubes. The use of non-isothermal conditions has now enabled us to fabricate long nano wires in fused silica tubing with a larger inner diameter than 10 μm. Mechanisms for the formation of such outgrowths are proposed.

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2. Experimental

Synthesis of 2-chloro-1,1,2-trifluoroethyl methyl ether by reacting 1,1,2-trifluoro-2-chloroethylene with methanol in the presence potassium hydroxide has previously been reported by Doyle *et al.* [27], and was performed accordingly. Loading of the fused silica capillaries (Polymicro, Phoenix, AZ, USA) with the ether has been described elsewhere [1]. In short, the ether was kept in a plastic vial, which was enclosed in a small stainless cylinder with two inlets. One of the capillary ends was inserted through one of the inlets of the container and dipped into the ether in the plastic vial. After sealing this inlet, the container was pressurized with helium via the other inlet. After a few seconds, the system was depressurized and the fluoro ether vial was removed. Subsequently, the setup was re-pressurized with helium, in order to distribute the plug of fluoro ether over the entire length of the capillary. When the plug reached the proximity of the outlet end of the capillary, the helium pressure was released, and the outlet end of the capillary was sealed with an acetylene/oxygen welding torch. The inlet of the steel container was then connected to a vacuum pump for 3–4 min, after which the capillary was also sealed at the inlet side. The length of the fluoro ether plug, which had remained intact, was determined by means of a microscope.

The sealed capillary was mounted in a hot oven and kept at constant temperature for 15–25 min. Experiments were carried out with the initial oven temperature ranging between 748 and 873 K. After this initial "hot start" period, the set-point temperature was decreased to 673 K and remained at that temperature for 10 h. The temperature profile was monitored using a thermocouple type K (Fluke Corp, WA, US), inserted in the center of the oven in proximity to the capillary. The thermocouple signal was cold junction-compensated by a circuit constructed in house (see Fig. 1) using a signal conditioner (DATEXEL, Florence, Italy) and a 2-terminal Zener (SGS-Thomson, AZ, US), and subsequently analog-digital converted (CB-68LP, National Instruments, TX, US). LabView^{TM} (National Instruments, TX, US) was utilized for data logging. The sampling frequency was set to 5 Hz. After removing the capillary from the oven and unsealing it, the capillary was flushed with helium at ambient temperature for about 5 min in order to remove residual gases. The result of the etching was studied by scanning electron microscopy (SEM) and in cases where nano wire outgrowth was observed, the capillaries were remounted in the oven and flushed with oxygen at 723 K for 5 h. In this way, residual carbon was oxidized and the fine structure of the nano wires could be revealed by means of a second SEM investigation.

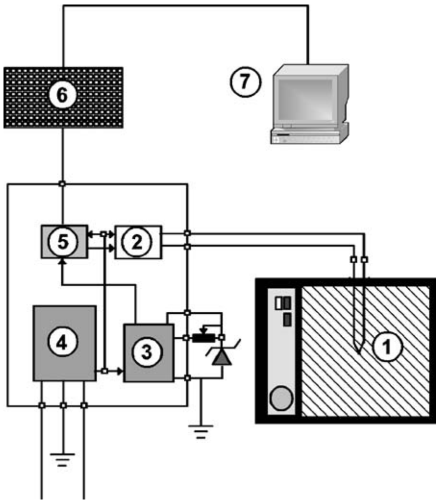

Figure 1 A schematic, showing the temperature logging system during the non-isothermal etching process. (**1**) the thermocouple type K, inserted in the oven, (**2**) signal amplifier, (**3**) cold junction compensator, (**4**) DC/DC convertion and power supply, (**5**) amplifier/analog out, (**6**) analog-digital conversion, and (**7**) the LabView^{TM} data logging system.

All SEM and TEM measurements were conducted using 1–2 mm long capillary pieces. In the case of SEM, the capillary pieces were gold coated, and carbon coated in the case of TEM, using a Polaron SEM Coating unit-PS3 sputter (Quorum Technologies, Newhaven, UK). Morphological investigations, using Scanning Electron Microscopy (SEM) in the secondary electron image mode, were performed with a Jeol 880 instrument (Jeol, Tokyo, Japan). SEM-EDS investigations were performed on the same instrument, with uncoated samples. The microstructure and degree of crystallinity of the nano wires was studied by using a Jeol 2000FX-TEM transmission electron microscope.

Since hazardous hydrogen fluoride is generated in the experiments, special care should be taken. All operations, including the heating and purging of the capillaries were therefore performed in a fume hood.

3. Results and discussion

In a previous report we described a technique for inducing nano wire growth in 2–5 μm ID fused silica capillaries [1]. Basically, the procedure involves a thermal breakdown of 2-chloro-1,1,2 –trifluoroethyl methyl ether at high temperature, which yields hydrogen fluoride, hydrogen chloride, carbon particles and water. After a period of 10–15 h under isothermal conditions at high temperature (typically 673 K), the nano wires were found to be present evenly around the internal circumference of the capillary. However, a section of the central capillary lumen always remained free of wires (see Fig. 2). Each nano wire ended with a spherical tip, and this tip was completely removed after flushing with oxygen at elevated temperature. Occasionally, depending on the concentration of etching agent and oven temperature, a carbon-containing epitaxial-like film was formed in the capillary instead of nano wires. In spite of many attempts, where etchant loading, temperature and etching time were varied, we were not able to obtain an even and reproducible outgrowth of nano wires, when the internal diameter of the capillary exceeded 10 μm. A typical result is shown in Fig. 3. Also the use of structurally similar fluoro/chloro carbon compounds as etching agents did not improve this situation. Thus, we came to consider our protocol as an artifact-like route for surface modification of only small bore (ID $\leq$5 μm) fused silica tubing.

However, in a particular experiment, using 10 μm ID capillaries, the starting temperature of the oven was

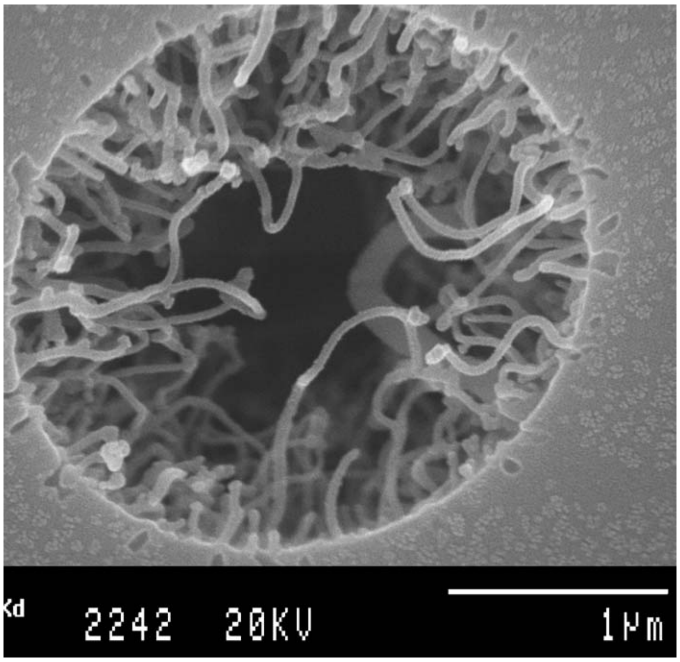

Figure 2 SEM micrograph of the cross section of a 2 μm ID fused silica capillary with isothermally grown nano wires. The capillary was filled with 31% of 2-chloro-1,1,2-trifluoroethyl methyl ether and subjected to 673 K for 14 h, and subsequently flushed with oxygen at 723 K for 5 h.

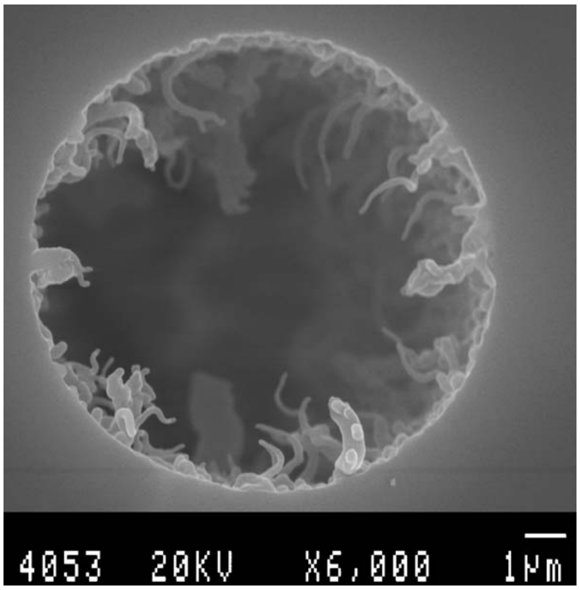

Figure 3 SEM micrograph of non-homogeneous and irregular nano wire outgrowth in a 10 μm ID fused silica. The capillary was filled with 26% (vol./vol.) of 2-chloro-1,1,2-trifluoroethyl methyl ether and was isothermally etched for 24 h at 723 K. Subsequently, the capillary has been flushed with oxygen for 5 h, at 723 K.

753 K for 10 min and then decreased to 673 K, and kept at this lower temperature during ca 10 h. Surprisingly, these non-isothermal conditions resulted in an entirely different type of nano wire outgrowth. The wires were much longer and protruded throughout the entire lumen of the capillary. The results were markedly different from our previously reported nano wire capillaries, an example of which is shown in Fig. 2. Thus, further experiments were carried out to find an optimal experimental window for preparation of the long nano wires. The temperature during the initial isothermal period was varied between 748 and 873 K, in increments of 25 K, and the etchant loading was varied between 18–38% (vol./vol.). These conditions were employed with capillaries of different inner diameters between 10–25 μm and lengths between 30–300 cm. The second isothermal plateau was kept at 673 K. All capillaries showed a similar, massive and regular nano wire outgrowth over the entire length of the tubing, as long as the 'hot start' period did not exceed 25 min. Extension of this period to 1 h yielded results similar to the morphology seen in Fig. 3. Temperatures higher than 823 K and 38% of filling with the ether resulted in exploded capillaries. The temperature profiles of the conducted experiments using the 'hot start' technique are shown in Fig. 4, and SEM micrographs of the resulting long

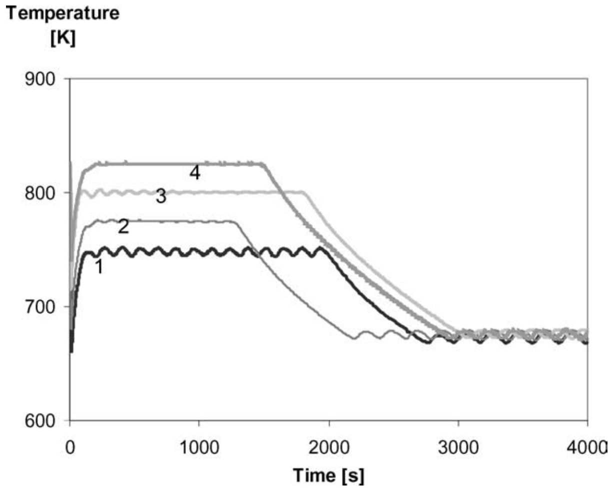

Figure 4 Four temperature profiles of the non-isothermal etching process, using 10 μm ID capillaries. Profile (1) starts at an oven temperature of 748 K for 30 min. Then the temperature is decreased under a period of 15 min, to 673 K. (2), (3) and (4) represent the corresponding temperature curves for the initial temperatures, T_0, of 773 (21 min), 798 (32 min) and 823 K (25 min) with transient periods of 18, 20 and 22 min respectively. Morphologies obtained with profile (1) and (4) can be seen in Fig. 5.

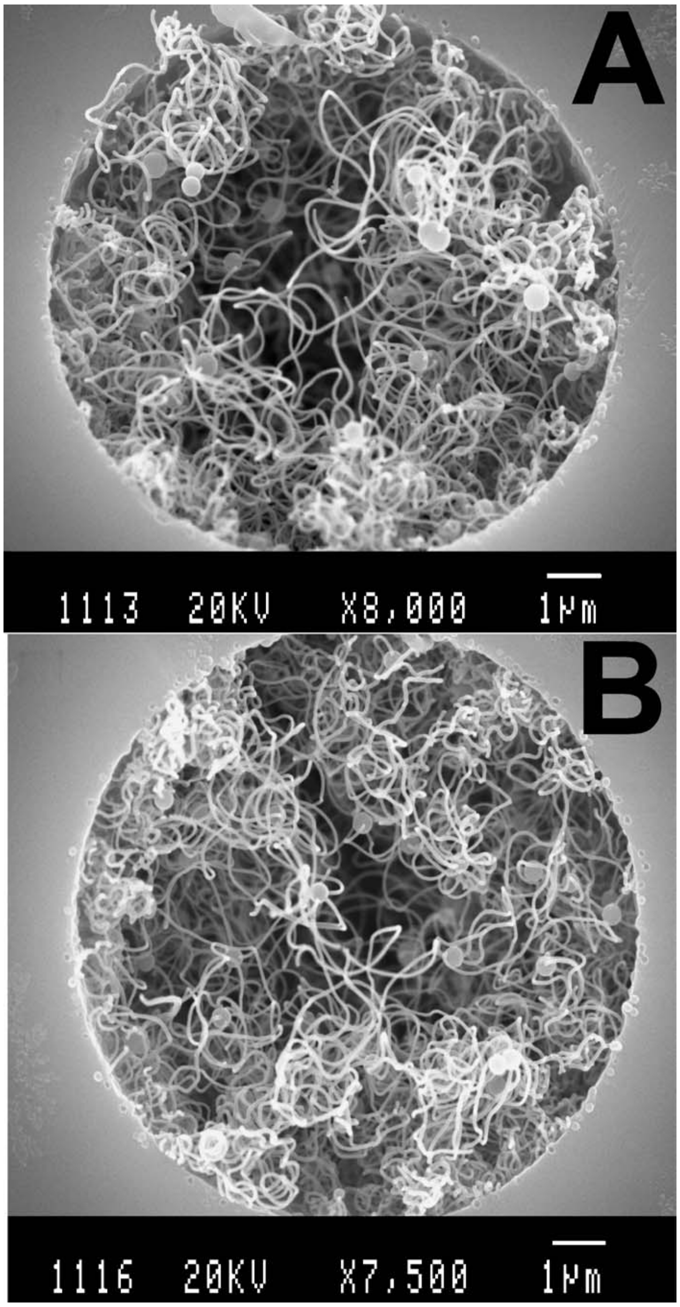

Figure 5 SEM-micrographs of 10 μm ID fused silica capillaries etched with the non-isothermal 'hotstart' protocol. Figure **A** shows silica nano wires obtained after using temperature profile (1) in Fig. 4, while Figure **B** shows the results obtained using temperature profile (4) in Fig. 4. Thus, essentially the same morphology is obtained for both these temperature profiles. Both capillaries were filled with 28% (vol./vol.) with 2-chloro-1,1,2-trifluoroethyl methyl ether. The capillaries have not been flushed with oxygen.

nano wires are shown in Fig. 5. The wires are heavily kinked and have a length of 5–15 μm. The widths of the wires are 10–50 nm and as can be seen, they occupy the entire capillary lumen.

Also, it can be clearly observed that globular carbon spheres have been formed. However, using the new 'hot start' non-isothermal procedure, the globular carbon particles are connected to several nano wires, while after isothermal etching employed in our previous work, the nano wires are not interconnected and each nano wire end has only one carbon particle (see Fig. 6). This has important implications regarding the possible mechanisms on the formation of the silica nano wires.

3.1. VLS-directed growth

In general, growth from the vapor phase entails the general process of taking atoms and molecules from the randomly distributed gas and incorporating them in a highly ordered structure. The associated reduction in entropy must therefore be balanced by a corresponding release of heat of condensation to the surroundings [28].

As for the growth mechanism of the silica nano wires, the SEM micrographs clearly suggest that a vapor-liquid-solid (VLS) mechanism is prevailing. The silica wires inside non-oxidized capillaries all end with a spherical tip when etched isothermally (see Fig. 6), which is typical for the VLS mechanism.

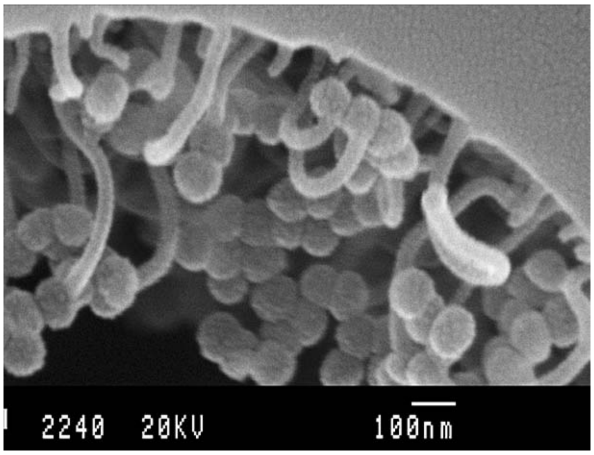

Figure 6 SEM micrograph of a 2 μm ID fused silica capillary, etched isothermally with 38% (vol./vol) of 2-chloro-1,1,2-trifluoroethyl methyl ether, for 16 h at 673 K. The spherical tips on each wire can be clearly observed. After oxidation, the spherical ends are completely removed (micrographs not shown).

The essential steps of the VLS mechanism are [29–31];

1. mass transport of the vapor components in the gas phase to the vapor-liquid interface.
2. chemical reaction on the vapor-liquid interface.
3. dissolution into and diffusion through the liquid. The surface of the liquid droplet might also serve as a favorable mass transport path for structural growth [32].
4. precipitation on the liquid-solid interface and subsequent incorporation into the structure lattice according to a two-dimensional growth theory.

The catalytic effects of the liquid droplet have generally been attributed to the high accommodation coefficient of the liquid surface, the intrinsic catalytic effect of liquid droplet and also to the decrease in activation energy of nucleation at the liquid-solid interface [32].

In the case of capillaries etched under the described non-isothermal conditions, the carbon particles seem almost perfectly spherical and may therefore not have been in contact with the capillary wall at all. These findings suggest that we have come across a phenomenon of VLS-growth where growth proceeds without any solid substrate for the nucleating droplet. The spherical carbon particles attached to the nano wires seem ‘arrested’ in the free space of the capillary lumen by nano wire entanglement before diffusing to the capillary wall (see Fig. 7). This would indicate that the kinetics of particle formation and the suggested hydrolysis of silicon tetra fluoride back to silica (described in the next chapter), are very fast under the conditions prevailing.

VLS-directed growth of amorphous SiO_x nano wires have previously been reported in various publications [4, 33–36]. It should be pointed out that the growth temperatures in these studies are in all cases considerably higher than the temperatures used under our non-isothermal etching process.

Carbothermal reduction synthesis at 1623 K [35] or prolonged (12 h) heat treatment of SiO_2/Si at 1673 K [36], have, e.g., been reported to yield silica based nano wires. Also heat treatment at 1453 K for two hours of an iron-containing silica xerogel mixed with silicon powder has been reported by Liang *et al.* to yield silica nano wires [34]. The elemental iron was used as the alloying element in the form of a $FeSi_2$-eutectic melt at the temperatures reported.

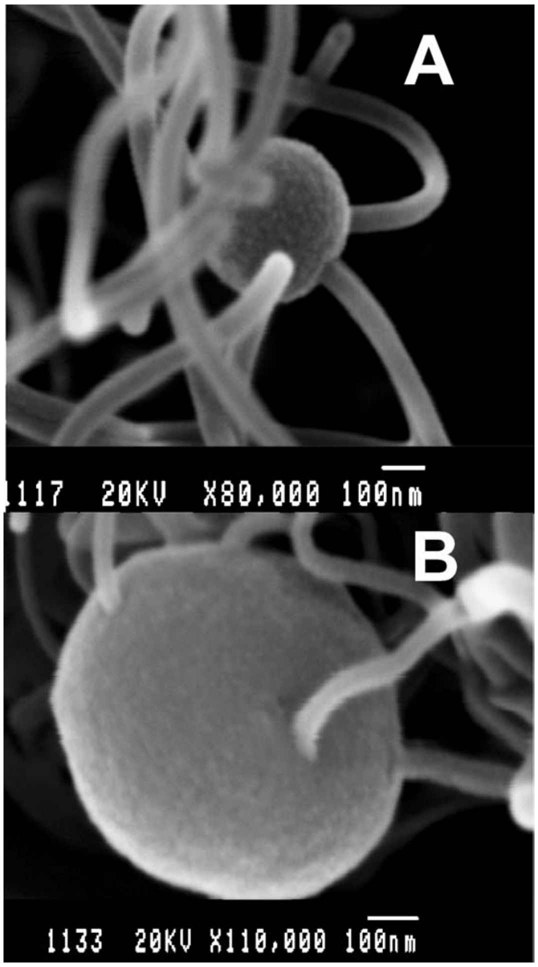

Figure 7 High magnification SEM micrographs of the spherical carbon particles nucleating the silicious vapor phase inside the fused silica capillary, under non-isothermal etching conditions. Note that several nano wires are connected to the same particle (B); in contrast to what is seen in Fig. 6. Since the carbon particles are distributed throughout the capillary lumen and are interconnected by several nano wires per particle, it seems as if the particles have not diffused to the capillary wall at all, but the fast nucleation/condensation of silica on the particle surface has arrested the particles in the free capillary lumen (A). The results were obtained by filling the capillary with 26% (vol./vol.) of 2-chloro-1,1,2-trifluoroethyl methyl ether, using the heating protocol of profile 3 (Fig. 4). The carbon particles are completely removed when the capillary is flushed with oxygen at 723 K for 5 h, while the silica nano wires remain intact.

3.2. Chemical transformations in the capillary

When the filled capillary is subjected to the elevated temperature, a rapid vaporization and pyrolysis of the fluoro ether occurs, which releases hydrogen fluoride and hydrogen chloride. The released hydrogen fluoride then attacks the silica surface, yielding hexafluosilicic acid and water [37, 38]. Details of the mechanism of hydrogen fluoride etching of an amorphous silica surface, performed at elevated temperatures and pressures are not fully understood. Habuka *et al.* [39] have reported that anhydrous hydrogen fluoride gas cannot etch silica at all if the temperature is below 1000 K. This finding is partly supported in several other publications [40–43]. During the etching, water is likely to be rapidly generated during the decomposition of the ether. With water present, the ionization of hydrogen fluoride into the active etchant HF_2^{-1} can therefore be initiated. The formation of silica nano wires inside the fused silica capillary as well as the chemistry involved has previously been discussed by us in detail [1]. The etchant precursor decomposes according to two reaction paths, one path not including any carbon-containing species and the other mainly dealing with the carbon based debris of the fluoro ether, as can be seen in Fig. 8. Along the 'inorganic' path, the hydrogen fluoride etching reaction proceeds to yield hexafluosilicic acid and silicon tetrafluoride. The hexafluosilicic acid decomposes into silicon tetrafluoride and hydrogen fluoride. The hydrogen fluoride formed in this reaction step continues to etch the capillary wall. The silicon tetrafluoride formed is then hydrolysed back to silicon dioxide, which again liberates hydrogen fluoride [44–47]. Thus, the etching and reformation of $SiO_2$is a sustained process under the conditions described.

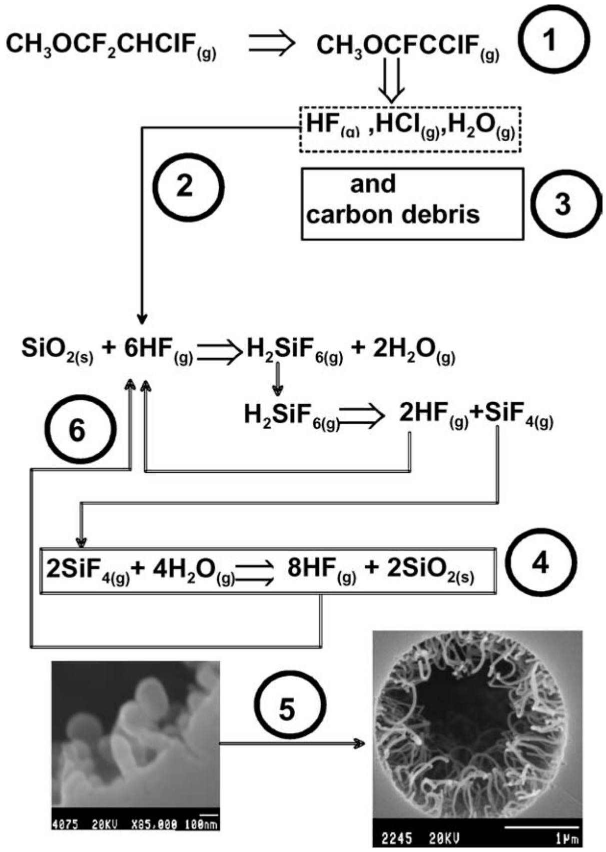

Figure 8 Schematic of the suggested chemistry inside the fused silica capillary during nano wire growth. (**1**) Due to the high temperature, 2-chloro-1,1,2-trifluoroethyl methyl ether decomposes and generates hydrogen fluoride, hydrogen chloride and water. (**3**) From the carbon backbone of the ether, carbon particles are formed. (**2**) Hydrogen fluoride attacks the fused silica surface, liberating additional water and forming hexafluosilicic acid. The hexafluosilicic acid decomposes to silicon tetrafluoride. (**4**) When this component diffuses to a carbon particle surface, hydrolysis of the silicon tetrafluoride yields a directed re-formation of the silica. The growth is directed to the backside of the carbon particles (**5**). Since hydrogen fluoride is released by the two last reactions (**6**), the nano wire growth is a sustained process (**5**).

Along the suggested 'organic' reaction path, the pyrolysis of the fluoro ether results in the formation of water and carbon primary particles. Particle agglomeration/aggregation yields nucleation sites for the hydrolysis products.

The fact that the pressure inside the capillary during etching is likely to yield supercritical conditions [1], complicates the model of nano wire growth considerably. Lespiaux *et al.* have previously described the nucleation of silicon carbide in a halogenated atmosphere as a function temperature and pressure, thus presenting a physicochemical model [48]. However, we believe that such a model approach can not be utilized in our case due to lack of equilibrium input data at these conditions.

3.3. EDS and TEM analysis

Energy dispersive spectroscopy (EDS) analysis, conducted on nano wire outgrowths, revealed the presence of both oxygen and silicon in the nano wires. However, for the low-Z elements silicon, oxygen, carbon and fluorine, the interaction volume and the sampling volume of the characteristic X-ray photons can often be considered to be 1 μm^3 or more [49]. The interaction volume of the incident electron beam is much larger than the volume of the nano wires. The EDS signal from the nano wires can therefore not easily be distinguished from the characteristic X-ray peaks of silicon and oxygen, generated by the bulk capillary material. In the absence of heavy elements, the results of EDS are therefore not fully reliable.

In order to further verify that the structures obtained did not consist of carbon, a stream of oxygen was guided through the wire-covered capillaries at 923 K for 6 h (or air at 1123 K for 3 h). After this harsh heat treatment, the wire structures remained intact. Since hardly any carbon based phases would persist after this treatment, we therefore conclude that the wires consist of silicon dioxide.

Additionally (after some initial difficulties), nano wires from the inside of a 30 μm ID capillary were transferred to a TEM-grid. The selected electron diffraction pattern was indicative for the morphology of the wires to be amorphous.

4. Conclusions

Our recently published work on isothermal etching is here complemented by new findings on silica nano wire growth in wide bore fused silica tubing. By the use of a time dependent, non-isothermal temperature profile, an essentially new morphology is accomplished in the capillary lumen. The nano wires produced using this scheme are different compared to the wires inside small bore fused silica tubing when isothermal heating is applied [1]. While the wires in the latter case are growing from fixed, individual spherical carbon particles attached to the capillary wall, the former nano wires show a pattern of very rapid nucleation and growth where one spherical carbon particle seeds several nano wires.

This results in a cross linked, open network of entangled wires with less fixed points at the capillary wall. The experimental domain for successfully growing this type of nano wires is, despite the use of a time dependent temperature profile, easily accomplished and large enough to be reproduced. As clearly shown in the figures, essentially the same morphology can be observed using the outer limits of the temperature profiles. From a fluidics point of view, the nano wires grown under the non-isothermal conditions seem to be more like a multi-flow path structure while the isothermally etched capillaries yield a mono-flow path type of structure, having an open core. We anticipate that the non-isothermally grown structure is more suitable for applications where a large increase in surface areas is advantageous, such as solid phase micro reactors and catalysis, including enzymatic reactions. The isothermally grown structure could be of considerable interest for open tubular liquid separations.

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