**Crystallization of Amorphous SiO₂ Microtubes Catalyzed by Lithium**

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Amorphous silica formed by thermally oxidizing silicon is commonly eligible for lithographic patterning or can be grown on patterned substrates. However, it is still a challenge to combine controlled microstructuring with controlled crystallization of SiO₂. Here, it is shown that traces of volatile lithium species transported through the gas phase catalyze the crystallization of silica integrated into common silicon microstructures. The selected crystallization temperature determines which polymorph forms. As an example, the formation of quartz, tridymite, and cristobalite microtubes by thermally oxidizing macroporous silicon is investigated. Lithium-induced crystallization may extend state-of-the-art silicon technology and yield nano- and microstructures consisting of different silica polymorphs, which are, in contrast to many functional oxides, nontoxic.

1. Introduction

Silica is a biocompatible and bioresorbable material that is, in its glassy state, widely used in silicon microtechnology. Commonly, only amorphous SiO₂ formed by thermal oxidation of Si is eligible for lithographic patterning or can be grown on patterned substrates. However, crystalline SiO₂ microstructures may show enhanced chemical and thermal stability with respect to their amorphous counterparts. They could be employed as resistant masks that facilitate plasma-etching processes commonly used to pattern Si wafers. Moreover, the silica polymorph quartz exhibits pronounced piezoelectricity.[1]

Therefore, quartz microstructures may be potential building blocks for miniaturized sensors and actuators in micro-electromechanical systems.[2,3]

Although amorphous SiO₂ nanostructures and microstructures with various morphologies have been fabricated in a well-controlled manner,[4–6] access to crystalline SiO₂ nano- and microstructures is still a challenge. Cristobalite nanowires were grown in the presence of carbon,[7] but mesopores in mesoporous silica vanish upon crystallization.[8] Other catalysts for the crystallization of silica glass are water,[9] noble metals,[10,11] and alkali ions.[12,13] The crystallization temperature determines which silica polymorph forms.[14]

Among the alkali metals, Li has been reported to be the most efficient catalyst for the conversion of amorphous silica glass into a crystalline phase, because the incorporation of Li results in the highest perturbation of the amorphous SiO₂ framework.[14,15] When lithium niobate microtubes are prepared inside the pores of macroporous Si[16–18] either by thermolysis of single-source precursors at 650 °C or by infiltration of LiNbO₃ melts at 1260 °C, quartz forms in the silica layer on the pore walls.[19,20] All the procedures described above start from glassy silica doped with metal atoms, or they require the presence of a bulk amount of catalyst in direct contact with the SiO₂ specimens to be crystallized. It is obvious that these approaches are tedious and costly or not compatible with state-of-the-art silicon technology and clean-room standards.

The exploitation of the properties of crystalline SiO₂ in low-dimensional systems having complex shapes such as tubes requires a simple and reliable process for the controlled crystallization of glassy silica. We report a one-step procedure meeting these requirements that involves the thermal oxidation of complex Si substrates and the crystallization of the SiO₂ thus formed catalyzed by Li, which is transported through the gas phase. Even though the nature of the volatile Li-containing species is yet unknown, the process yields well-defined single-crystalline microtubes. No direct contact between the Si specimen and the Li source is necessary. As examples, we have investigated the formation of quartz, tridymite, and cristobalite microtubes obtained from macroporous Si with a pore diameter of 1 μm and pore depths ranging from 100 to 150 μm.
2. Results and discussion

Figure 1 shows a series of scanning electron microscopy (SEM) images of macroporous Si containing crystalline SiO$_2$ microtubes crystallized at 1200 °C for 2 h, 6 h, 12 h, and 24 h. The SiO$_2$ microtubes appear as bright annuli surrounding the pore openings. As expected, their thickness increased with increasing annealing time from ca. 200 nm after 2 h (Fig. 1a) to ca. 280 nm after 6 h (Fig. 1b) to ca. 360 nm after 12 h (Fig. 1c). After annealing times of more than 24 h, the SiO$_2$ microtubes impinged upon each other and no further oxidation of the remaining Si pillars between three adjacent SiO$_2$ microtubes could be observed (Fig. 1d). The conversion of Si into SiO$_2$ leads to an increase in volume by 125 % per Si atom.[21] It is obvious that the SiO$_2$ that would form in the course of a complete oxidation of the Si matrix cannot be accommodated in the confined space between the SiO$_2$ microtubes. Therefore, the growth of the oxide layer is self-limited. For a given crystallization time, the thickness of the formed silica layer is uniform over the entire specimen.

We crystallized macroporous Si in air at temperatures of 1050, 1100, and 1200 °C, respectively, in the presence of small amounts of LiNbO$_3$. In this temperature range, the transition from a preferred formation of quartz at lower crystallization temperatures to the preferred formation of cristobalite at higher crystallization temperatures can be observed. As discussed below, considerable amounts of the third low-pressure polymorph of SiO$_2$, tridymite, and cristobalite form. Figure 2 shows SiO$_2$ microtubes crystallized at 1050 °C for 2 h, which we released either partially or completely by etching the residual Si with 30 wt % aqueous KOH solution at 80 °C. After an etching time of 15 min, approximately 30 μm of the microtubes were liberated, whereas the lower microtube segments were still embedded in the Si matrix (Fig. 2a). After etching for 90 min, the silica microtubes were completely released. Their high mechanical stability prevented them from breaking during the preparation procedure. Even in SEM images containing a large number of silica microtubes, no short segments and broken tubes appeared (Fig. 2b). Figure 2c is a representative SEM image of a single silica microtube with an aspect ratio (length/diameter) of 140:1, corresponding to that of the pores in the macroporous Si. The walls of the microtubes are smooth and free of defects. Figure 2d shows a transmission electron microscopy (TEM) image of a ultrathin slice containing a section across a SiO$_2$ microtube broken into 200–500 nm long segments because of the mechanical stress exerted on the specimen during the preparation of the slices. The wall thickness of about 80–90 nm is significantly smaller than that of the sample crystallized at 1200 °C for 2 h (Fig. 1a). The apparent brittleness of the SiO$_2$ microtubes is indicative of their crystalline nature.

X-ray diffraction (XRD) on ensembles of silica microtubes crystallized for 2 h revealed that, depending on the crystallization temperature, low-pressure polymorphs of SiO$_2$, quartz, tridymite, and cristobalite form. Figure 3a–c shows XRD patterns of released SiO$_2$ microtubes deposited on silicon wafers. We crystallized them at 1050 (Fig. 3a), 1100 (Fig. 3b), and 1200 °C (Fig. 3c). The (101) reflection of cristobalite at 2θ = 21.9° (indexed according to the International Centre for Diffraction Data (ICDD) entry 76-0937) appears in all three diffraction patterns. However, strong (100) and (011) reflections of quartz appear in Figure 3a at 2θ = 20.8° and 26.6° (indexed according to ICDD entry 88-2487), thus revealing that
cristobalite and quartz coexist in samples crystallized at 1050 °C. Besides peaks originating from cristobalite and quartz, the XRD pattern of the sample crystallized at 1100 °C also contained a weak (100) reflection of tridymite at 2θ = 20.5°, a weak (101) reflection of tridymite at 2θ = 23.2°, and a weak (102) reflection of tridymite at 2θ = 30.0° (indexed according to ICDD entry 89-3141) (Fig. 3b). Therefore, all three low-pressure polymorphs of SiO2 are present in this sample. The relative intensity of the cristobalite reflections increases along with the crystallization temperature. The XRD pattern of SiO2 microtubes crystallized at 1200 °C contains strong cristobalite peaks but no reflections of quartz and only a weak (100) reflection of tridymite at 2θ = 20.5° (Fig. 3c).

We could also evidence the formation of quartz, tridymite, and cristobalite by the evaluation of selected-area electron diffraction (SAED) patterns of segments of the SiO2 microtubes crystallized for 2 h. Figure 4a shows a TEM image of a segment of a microtube crystallized at 1200 °C that exclusively consists of quartz (space group P3221). The presence of a single set of Bragg reflections in the corresponding SAED pattern (Fig. 4b) confirms its single-crystalline nature. A single-crystal microtube segment crystallized at 1100 °C (Fig. 4c) consists of tridymite (space group P63/mmc). Again, the corresponding SAED pattern contains only a single set of diffraction spots (Fig. 4d). Cristobalite (space group P41212) formed in a tube segment crystallized at 1200 °C, as the evaluation of the corresponding SAED pattern (Fig. 4f) revealed; even though more than one set of Bragg reflections appeared, it is obvious that the tube wall contains large single-crystalline areas. We analyzed the elemental composition of the walls of the SiO2 microtubes by electron energy-loss spectroscopy (EELS, spectra not shown) but could not detect Li. This indicates that the concentration of this element is below one atomic percent, which is the resolution limit of the EEL spectrometer used.

The formation of pure quartz on the pore walls of macroporous Si covered with LiNbO3 has been observed at temperatures as low as 650 °C.[19] In the temperature range considered here, a transition from the formation of quartz to the formation of cristobalite occurs as the crystallization temperature is increased. The results obtained for macroscopic ensembles of SiO2 microtubes by using XRD and for segments of single SiO2 microtubes from the SAED patterns are consistent. At
1050 °C, reflections originating from quartz are the dominant features in the XRD pattern, and SAED investigations reveal the presence of single-crystalline microtube segments consisting of quartz. In the XRD pattern of the sample crystallized at 1100 °C, reflections of all three low-pressure polymorphs of SiO2 show up. The microtube segments investigated by using TEM were again single-crystalline and consisted only of one modification, for example tridymite (Fig. 4c and d). At 1200 °C the SiO2 predominantly crystallized into cristobalite. Even though macroscopic ensembles of the SiO2 microtubes may contain different crystal modifications, the microtubes consist of single-crystalline segments. The TEM investigations moreover revealed the absence of amorphous SiO2.

The presence of traces of volatile Li-containing species in the atmosphere of the furnace used for the thermal oxidation of the macroporous Si is actually crucial to the crystallization of the SiO2 thus formed. We found no crystalline SiO2 in macroporous Si annealed in the absence of Li but otherwise under the same conditions. For example, Figure 5 shows the XRD pattern of macroporous Si annealed at 1100 °C, which only contains a broad diffuse halo that we ascribe the presence of amorphous SiO2.

The expansion in volume associated with the conversion of Si into SiO2,[21] results in the occurrence of mechanical stress at the Si/SiO2 interface. The oxidation of Si in a spherical geometry is characterized by complex processes on the nanometer scale.[22] The presence of a concave curvature as in macroporous Si results in a pronounced retardation of the oxide growth with respect to planar oxidation.[21,23–27] Kao et al. attributed this phenomenon to viscous stress in the oxide layers associated with nonuniform mechanical deformation.[24] Whereas in planar systems only stress components parallel to the Si/SiO2 interface exist in the newly formed SiO2 layer, stress normal to the Si/SiO2 interface also occurs in concave systems. Therefore, a destabilization of the amorphous SiO2 framework due to the non-planar nature of the Si/SiO2 interface may be considered as an additional cause of crystallization. To investigate the influence of the curvature, we subjected smooth (100)-oriented Si wafers to the same procedures as the macroporous Si. Oxidizing the wafers in a furnace in the absence of any Li source exclusively yielded amorphous SiO2, whereas cristobalite partially formed on a wafer thermally oxidized at 1250 °C for 2 h in the presence of some LiNbO3. The corresponding XRD pattern shown in Figure 6 contains the (101), (102), and (200) reflections of cristobalite at 2θ = 21.9°, 2θ = 31.3°, and 2θ = 36.0°, respectively (indexed according to ICDD entry 76-0937). A weak (100) reflection of tridymite shows up at 2θ = 20.5° (indexed according to ICDD entry 89-3141). Moreover, the kinematically forbidden (200) reflection of Si, which may occur when the Si lattice is subjected to distortions,[19,20] appears at 2θ = 32.8°.

The bright-field TEM image (Fig. 7a) and the corresponding dark-field TEM image (Fig. 7b) of a cross-sectional specimen containing the SiO2 film connected to the underlying Si wafer revealed a film thickness of about 800 nm. This is more than twice the thickness of the SiO2 layers formed in macroporous Si after annealing at 1200 °C for 24 h in the presence of a Li source (Fig. 1d). A typical SAED pattern of the SiO2 film covering an area of ca. 0.5 μm² (Fig. 7c) contains a set of Bragg reflections that can be ascribed to cristobalite (space group P4₁2₁2, indexed according to ICDD card no. 76-0937). However, at annealing temperatures below 1250 °C no crystalline phase formed in the SiO2 layers on the smooth Si wafers, and above 1250 °C no quartz was found. In macroporous Si, the combination of the catalytic properties of Li and the stress occurring in the tubular geometry distinctly influences the growth and the cristallization of silica in two regards. On the one hand, the increase in the thickness of the silica layer is slowed down. On the other hand, crystallization sets in at significantly lower temperature than in the absence of either Li or curved Si/SiO2 interfaces. As a result, not only cristobalite but also quartz can be obtained by varying the crystallization temperature.
of SiO$_2$ in connection with Si microstructures might yield highly resistive silica masks that facilitate dry-etching processes or enhance the chemical and mechanical stability of miniaturized building blocks. Moreover, quartz microtubes are potential nanoactuators because of the piezoelectric properties of this silica polymorph.

4. Experimental

The fabrication of macroporous Si is described elsewhere [16,17]. In brief, lithographically pre-patterned, (100)-oriented n-type silicon wafers are used as substrates. Transferring the lithographic pattern into the silicon by photo-electrochemical etching yields a monodomain of pores with a sharp size distribution [16,17]. The order imposed by lithography is retained upon etching. The dispersity of the pore-diameter distribution is less than 1%.

We placed macroporous Si and a crucible containing one or two droplets of a 5 wt% solution of LiNb(OC$_3$H$_7$)$_6$ in isopropyl alcohol (Alfa Aesar) in a furnace and heated the samples to 1050, 1100, or 1200 °C, respectively, at a rate of 20 K min$^{-1}$ in the case of the specimens seen in Figure 1, and at a rate of 10 K min$^{-1}$ in the case of all other specimens. The samples were kept at the selected crystallization temperature for 2 h except those seen in Figure 1. All samples were cooled to room temperature at a rate of 1 K min$^{-1}$. The entire procedure was carried out in air under static conditions.

For the SEM investigations of SiO$_2$ microtubes embedded into macroporous Si and released SiO$_2$ microtubes deposited on highly conductive Si wafers, we used a field-emission scanning electron microscope (JEOL JSM 6300F) operated at accelerating voltages between 5 and 8 kV. Completely released SiO$_2$ microtubes were obtained by etching the Si with a 30 wt% aqueous KOH solution at 80 °C. The SiO$_2$ microtubes thus liberated were washed several times by centrifuging, removing the supernatant liquid, and adding deionized water.

The TEM images in Figures 1 and 3 were obtained using a JEM 1010 transmission electron microscope operated at 100 kV. Aqueous suspensions of released tubes were directly dropped onto copper grids coated with a holey carbon film. To prepare the cross-sectional specimen of a silicon wafer oxidized for 2 h at 1250 °C in the presence of LiNbO$_3$, a) the bright-field image; b) corresponding dark-field image; and c) typical SAED pattern (zone axis <211>, (111) and (0-11) reflections of cristobalite are marked).

3. Conclusions

We have demonstrated that Li-induced crystallization of SiO$_2$ allows the integration of quartz and cristobalite layers into microstructured Si building blocks. As an example, we prepared crystalline SiO$_2$ microtubes by thermally oxidizing macroporous silicon in the presence of a Li source. The Li was transported through the gas phase in the form of an unknown volatile species. However, we obtained SiO$_2$ microtubes consisting of single-crystalline segments. Their wall thickness, which is adjustable by the applied annealing time and the applied annealing temperature, is uniform at a macroscopic scale. No doping of the specimen to be oxidized, no direct contact with the Li source, and no bulk amount of the Li source are required. Li unambiguously catalyzes the crystallization of silica. Compared with a planar geometry, the stress caused by the curvature of the pore walls in macroporous Si retards the growth of SiO$_2$ upon thermal oxidation but facilitates its crystallization. In a tubular geometry, Li-induced crystallization sets in at lower temperatures than in planar systems. Therefore, quartz microtubes can be obtained from macroporous Si at crystallization temperatures where planar systems do not crystallize at all. At the higher crystallization temperatures required for planar systems cristobalite forms exclusively. Released SiO$_2$ microtubes with a diameter of 1 μm and a wall thickness of 80–90 nm had aspect ratios of 100:1 to 150:1, corresponding to those of the template pores. The crystallization...