CHAPTER VI

Modification of Macroporous Silicon by Templated Thermal Conversions

As we introduced in chapter 3, the pores of macroporous silicon are arranged in either a hexagonal or quadratic lattice characterised by a sharp pore diameter distribution, forming a monodomain that may extend several cm$^2$. Specific defect structures such as linear and bent waveguides, Y-branches and microresonators can be implemented into this two-dimensional (2D) photonic bandgap material [150]. Macroporous silicon has been employed as a template for the fabrication of tubular structures [13] [23] [25]. Modification of macroporous silicon by functional oxide microtubes will result in hybrid systems consisting of billions of aligned functionalized channels, which have a great potential for the design of micrometer-scale, functional optical components in micro-devices. Conventional approaches to move functional materials into the pores are mainly based on the conversion of precursors [76] [78] [126], and the tubes thus obtained are grainy and of poor mechanical stability. Moreover, the controlled incorporation of dopants, and the control over the stoichiometry of the wall material is difficult to achieve. To overcome these drawbacks, we introduced a so called high temperature melt wetting approach. This is a modified templated high-temperature conversion approach that involves infiltration of the porous template directly with the melt of the target material. As an example, we infiltrated macroporous silicon with a congruent LiNbO$_3$ melt containing 0.3 mol% Er, as discussed in section 6.1. An interesting phenomena appeared in the fabrication of LiNbO$_3$ and Er:LiNbO$_3$ microtubes. There are crystalline reflections of SiO$_2$ in the XRD patterns besides those of LiNbO$_3$. We assume the crystallization of amorphous SiO$_2$ covering the pore walls is induced by trace amount of lithium, which volatilized from the LiNbO$_3$ melt at elevated temperature during the annealing process. Thus, another way to modify macroporous silicon by microtubes is proposed: preparation of crystalline SiO$_2$ microtubes in the macroporous silicon by offering lithium to induce crystallization of amorphous SiO$_2$. 
6.1 LiNbO$_3$ and Er:LiNbO$_3$ microtubes by high temperature melt wetting

Doping host systems with rare earth elements yields functional materials with superior optical properties. Trivalent erbium, Er$^{3+}$, is of particular interest, because the sharp optical intra-4f transitions from the first excited state $^4$I$_{13/2}$ to the ground state $^4$I$_{15/2}$ at 1.53 $\mu$m coincide with the transmittance maximum of silica-based fibers \[151\] \[152\]. However, the integration of such dopant/host systems into device architectures has remained a problem. Only few examples for Er$^{3+}$-doped 1D nanostructures and microstructures have been reported to date: for example, as-grown silicon \[153\] and germanium \[154\] nanowires were exposed to a volatile erbium compound. The challenge remains to control the doping level, and to integrate Er$^{3+}$-doped 1D building blocks into functional device architectures based on Si microstructures, such as macroporous Si. In our experiments, Er$^{3+}$-doped LiNbO$_3$ microtubes were fabricated by infiltrating of macroporous silicon with a congruent LiNbO$_3$ melt containing 0.3 mol% Er.

6.1.1 Fabrication of LiNbO$_3$ and Er:LiNbO$_3$ microtubes

To obtain the Er:LiNbO$_3$ microtubes, we infiltrated macroporous silicon with a congruent LiNbO$_3$ melt containing 0.3 mol% Er. At first, Er-doped LiNbO$_3$ single crystals were grown along the c-axis in air from the congruent melt by the conventional Czochralski method \[155\] and manually milled using an agate mortar. Subsequently, we covered macroporous Si (pore diameter 1 $\mu$m, pore depth 100 $\mu$m) with a thin layer of the powder thus obtained. The samples were annealed at 1260°C just above the melting point of single-crystalline LiNbO$_3$ for 2 hours, and cooled to 1050°C at a rate of 0.1°C/min. To eliminate residual internal stress and defects, this temperature was kept for 3 hours, before the samples were cooled to room temperature at a rate of 5°C/min. All steps were performed in air. No external driving force was applied to pull the melt into the pores. The residual material on the template surface was carefully removed by mechanical polishing. Optionally, the macroporous Si can be selectively etched with aqueous 30 wt-% KOH at elevated temperatures to release the Er:LiNbO$_3$ microtubes.
6.1.2 Morphology and structural characterization of LiNbO$_3$ and Er:LiNbO$_3$

microtubes

Figure 6.1 shows a SEM picture of the polished surface of macroporous Si containing Er:LiNbO$_3$ microtubes. Their walls appear in a brighter contrast than the surrounding Si matrix. An array of partially released, aligned Er:LiNbO$_3$ microtubes connected with macroporous Si acting as a support is seen in Figure 6.1b, and completely liberated Er:LiNbO$_3$ microtubes deposited on a Si wafer are shown in Figures 6.1c and 6.1d. Their walls are smooth and virtually free of defects. Their aspect ratio amounts to 100 corresponding to that of the template pores. Therefore, the Er:LiNbO$_3$ melt must form a uniform wetting layer completely covering the pore walls of the macroporous silicon template. Powders of released Er:LiNbO$_3$ microtubes contain no short tube fragments (Fig. 6.1c, 6.1d). This indicates that their considerable mechanical stability prevents the Er:LiNbO$_3$ microtubes from breaking in the course of the preparation procedure.

![SEM images Er:LiNbO$_3$ microtubes. (a) Er:LiNbO$_3$ microtubes within macroporous Si after polishing the template surface. (b) Array of aligned Er:LiNbO$_3$ microtubes partially embedded in macroporous Si after partially etching the template. (c),(d) Completely liberated Er:LiNbO$_3$ microtubes deposited on a Si wafer.](image-url)
A representative bright-field TEM image of an Er:LiNbO$_3$ microtube segment is shown in Figure 6.2a, and the corresponding selected area electron diffraction (SAED) pattern in Figure 6.2b. Only one set of spots is seen, evidencing the single-crystalline nature of the tube wall. At slow cooling rates as applied here, a small number of nuclei, formed at high nucleation temperatures, will initiate crystallization. Under these conditions, the growth of extended single-crystalline entities can be expected. However, twinned structures [156] may form, when the centrosymmetric high-temperature phase of LiNbO$_3$ is converted into the non-centrosymmetric low-temperature phase at the Curie point of 1160°C. Therefore, we assume that the Er:LiNbO$_3$ microtubes consist rather of single-crystalline segments than of one single crystalline entity. Figure 6.2c shows an ultra-thin slice with a thickness of a few tens of nm, as determined from its interference colour, containing a cross-section across a Er:LiNbO$_3$ microtube embedded in epoxy resin along its long axis. Figure 6.2d shows correspondingly a cross-section along a tube. The tube walls, which were partially damaged because of the mechanical stress imposed during the sample preparation, have a uniform thickness of about 100 nm. If the mechanical failure predominantly occurs at grain boundaries, the intact wall segments should correspond to single crystalline domains. We estimate their extension in the direction of the tubular long axis to be of the order of several hundreds of nm.

6.1.3 X-ray diffraction of LiNbO$_3$ and Er:LiNbO$_3$ microtubes

XRD scans of macroscopically aligned Er:LiNbO$_3$ microtubes located within the pores of polished macroporous Si were measured in the reflection mode (Fig. 6.3a). The sample surface was inclined by 5° with respect to the plane defined by the incident beam and the detector. The kinematically forbidden (200) reflection of the (100) oriented Si template at 32.8°, which occurs when macroporous Si is annealed in air, would otherwise coincide with the (104) peak of LiNbO$_3$ [126]. It is well known that thermal oxidation of macroporous Si imposes considerable mechanical stress on Si forming the pore walls [157]. Solely annealing macroporous silicon in argon/air environment does not result in the occurrence of lattice distortions abrogating the extinction of the (200) (Fig. 6.4a), whereas, a sharp Si (200) peak appears in the XRD pattern when the macroporous silicon is annealed in the presence of lithium (Fig. 6.4b). Hence, the Si lattice must have been distorted upon the formation of the crystalline LiNbO$_3$ tubular structures on the pore surface of macroporous silicon (Fig. 6.3). In Figure 6.3, the XRD pattern contains the characteristic reflections of LiNbO$_3$ (space group R3c, JCPDS entry 78-0250). The (210)/(011) double peak at
**Figure 6.2:** TEM images of Er:LiNbO$_3$ microtubes. (a) Single Er:LiNbO$_3$ microtube. (b) Corresponding SAED pattern. The (012) and (116) diffraction spots of rhombohedral LiNbO$_3$ are denoted, the growth direction of the tube is (012). (c) and (d) Ultra-thin section of a Er:LiNbO$_3$ microtube embedded in epoxy resin along its long axis.
21.4° - 21.6° (JCPDS entry 26-1176) of the lithium-deficient phase LiNb$_3$O$_8$, possibly formed as the product of an interfacial reaction [158] [159] between the LiNbO$_3$ and the silicon oxide covering the pore walls, also shows up.

A third set of reflections is found too and can be ascribed to trigonal quartz (space group P3$_2$1, JCPDS entry 85-0794), which forms as the silica layer on the pore walls crystallises during annealing in air [126]: the (100) reflection at 20.6°, and the (110) peak at 36.5°. The occurrence of weak (200) and (111) peaks of cubic Si (JCPDS entry 27-1402) at 28.5° and 31.6° indicates that crystallites with a deviating orientation have formed within the (100) oriented Si matrix. Otherwise, the peaks would not appear in the geometry up used for the measurements (Fig. 6.4a). We assume the crystallization of amorphous SiO$_2$ is induced by Li traces evaporated form the LiNbO$_3$ melt at elevated temperatures [160] [161]. The details are discussed in section of lithium-induced crystallization of amorphous SiO$_2$ microtubes (section 6.2). XRD investigations on released LiNbO$_3$ microtubes deposited a (100)-oriented Si wafer, however, revealed the absence of quartz and Si after the selective etching of the template by KOH 30 wt-% 90°C 2h. Only LiNbO$_3$ and weak LiNb$_3$O$_8$ peaks show
up (Fig. 6.3b). The relative peak intensities of both patterns are similar to those of the LiNbO$_3$ powder pattern of a milled single crystal fabricated by the Czochralski method (Fig. 6.3c). Macroscopic ensembles of aligned Er:LiNbO$_3$ and LiNbO$_3$ tubes show therefore no apparent texture.

![Figure 6.4: XRD patterns of macroporous silicon (Dp = 1 µm; Lp = 100 µm), alkali annealed (a) in air and (b) in the presence of lithium at 950°C for 2h. In the latter case, a starting (200) reflection of Si appears.](image)

**6.1.4 Optical properties of Er:LiNbO$_3$ microtubes**

The room temperature PL spectra of Er:LiNbO$_3$ microtubes and bulk Er:LiNbO$_3$ show essentially the same features. The spectra of Er:LiNbO$_3$ microtubes embedded within the pores of the macroporous Si (Fig. 6.1a), released Er:LiNbO$_3$ microtubes deposited on an Si wafer (Fig. 6.1b), and bulk Er:LiNbO$_3$ in the range from 1450 and 1600 nm are presented in Figures 6.5a, b, c, respectively. In all cases a pronounced $^4$I$_{13/2} \rightarrow ^4$I$_{15/2}$ transition at 1.53 µm appears. The satellite peaks at 1490, 1513, 1547, 1562, 1575, and 1606 nm, respectively, represent the transitions among the multiplet manifolds. This energy-level splitting caused by the crystal field of the matrix indicates that the active Er$^{3+}$ centers are located within a well-defined crystalline environment. The PL of the visible range of Er:LiNbO$_3$ microtubes embedded in the template (Fig. 6.5d), of released Er:LiNbO$_3$ microtubes deposited on a Si wafer (Fig. 6.5e), and of bulk Er:LiNbO$_3$ (Fig. 6.5f) indicates that a rapid non-radiative de-excitation from the excited state $^2$K$_{15/2}$ to the $^4$S$_{3/2}$ state takes place. Among the different emissions that can be observed, the $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$ (550 nm) and the $^4$S$_{3/2}$
$^4\text{I}_{13/2}$ (860 nm) transitions are the most intense ones. The $^4\text{I}_{11/2}$ state is populated too, predominantly via non-radiative channels, so that the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (980 nm) transition can be detected.

![Figure 6.5: Room temperature photoluminescence emission spectra.](image)

(a) IR range from Er:LiNbO$_3$ microtubes embedded in macroporous Si. (b) IR range from released Er:LiNbO$_3$ microtubes deposited on a Si wafer. (c) IR range from bulk Er:LiNbO$_3$. (d) Visible range from Er:LiNbO$_3$ microtubes embedded in macroporous Si. (e) Visible range from released Er:LiNbO$_3$ microtubes deposited on a Si wafer. (f) Visible range from bulk Er:LiNbO$_3$.

### 6.1.5 High-temperature melt wetting

The question arises as to how the Er$^{3+}$-doped LiNbO$_3$ move into the template pores? Vacuum melting combined with high-pressure injection of melts of various inorganic materials into the nanopores of anodic alumina [162] was employed to obtain solid nanowires. However, no external driving force is required to infiltrate liquid Er:LiNbO$_3$ into macroporous Si. The pore walls of macroporous silicon are covered with a native silica layer which has a quiet high surface energy of the order of 520
mN/m \[163\]. The surface energy of molten LiNbO\(_3\), which lies in the range from 310 to 320 mN/m \[164\], may be sufficiently low for a complete wetting of the solid pore walls. Moreover, the interfacial reaction leading to the formation of LiNb\(_3\)O\(_8\) \[158\] \[159\], the presence of which has been evidenced by XRD (Fig. 6.3a,b), possibly triggers chemical spreading. The second interesting phenomenon is the stability of the liquid cylindrical Er:LiNbO\(_3\) layer covering the pore walls. A general mechanism for the infiltration of pores and capillaries with liquids involves the initial formation of such a wetting film \[165\] \[166\]. However, cylindrical liquid films are susceptible to hydrodynamic instabilities \[167\], leading to the formation of menisci (snap-off). Their interfaces move in opposite direction as more liquid moves into the pore. Eventually, this results in the complete filling of the pore volume with the liquid \[165\]. In case of disordered polymer melts the infiltration stops after the formation of the wetting layer \[25\] \[168\]. This has been attributed to the bulkiness of the macromolecules: The wetting layer comprises only a monolayer of molecules, each of which is in contact with the pore walls. The reason for the stability of the liquid cylindrical Er:LiNbO\(_3\) films may be the well-known presence of mesoscopic cluster structures within LiNbO\(_3\) melts \[169\] \[170\]. The intrinsic short-range order imposed by these clusters would be disturbed by the occurrence of instabilities so that their growth might be suppressed.

In this section, the preparation of Er\(^{3+}\)-doped lithium niobate (LiNbO\(_3\)) microtubes consisting of single-crystalline segments within the pores of macroporous silicon \[57\] \[65\] by infiltration of Er:LiNbO\(_3\) melts was discussed. Both embedded and released Er:LiNbO\(_3\) microtubes show the characteristic photoluminescence of Er\(^{3+}\):LiNbO\(_3\) which exhibits rapid non-linear optical response behaviour, low switching power and broad conversion bandwidth and is therefore an attractive host system \[171\] \[172\]. Si-based microstructures combined with the functionality of Er:LiNbO\(_3\) are potential components for complex device architectures. Moreover, the so called high temperature melt wetting approach presented here may be applicable to other nano- and microstructures than macroporous Si, such as mesoporous Si, artificial opals and their inverse counterparts. Even though the underlying physico-chemical phenomena are not fully understood, the wetting of silica-based micro- and nanostructures with Er:LiNbO\(_3\) should have a great potential for the design of micro-scaled, functional optical components.
6.2 Lithium-induced crystallization in amorphous SiO$_2$ microtubes

Many minerals are known to have the chemical composition SiO$_2$. The silica (SiO$_2$) minerals include quartz, tridymite, cristobalite, coesite, stishovite and several others. The polymorphs have different structures, with different symmetries and different physical properties. Each of the polymorphs has both an $\alpha$- and a $\beta$-form. The $\alpha$-form distorted versions of the $\beta$-forms and occurs at lower temperatures and have lower symmetry. Quartz is the most important and best known of silica. It goes through a structural transitions from $\alpha$-phase (or low-quartz) to the $\beta$-phase (or high-quartz) at 573°C. Phase transition of $\beta$-form quartz to $\beta$-from tridymite occurs at 870°C. Silica (SiO$_2$) is a biocompatible and bioresorbable material. Especially quartz exhibits pronounced piezoelectric behaviour [173] and is therefore a promising raw material for miniaturized components for sensors, actuators and micro-electromechanical systems (MEMS).

Although amorphous SiO$_2$ nanostructures and microstructures with various morphologies have been fabricated in a well-controlled manner [174], the access to crystalline SiO$_2$ nano- and microstructures is still a challenge. This is particularly the case for complex structures such as tubes, which are of considerable interest because of their intrinsic anisotropy. Tubular structures consisting of amorphous SiO$_2$ are easily accessible by thermal oxidation of the pore walls of macroporous Si. However, to exploit the properties of crystalline SiO$_2$ in low-dimensional systems, a simple and reliable process for the controlled crystallization of glassy silica is required. We solved this problem by a simple and easy process. Crystalline SiO$_2$ microtubes were accomplished in macroporous silicon using a so-called lithium-induced crystallization approach, in which trace of lithium serve as catalyst in the crystallization process.

6.2.1 Lithium-induced crystallization in SiO$_2$

Commonly, only amorphous silica forms by thermal oxidation of crystalline silicon is either in unpatterned or in lithographically patterned form, or can be grown on patterned substrates. Cristobalite nanowires were grown in the presence of carbon [175]. Mesopores in mesoporous silica vanish upon crystallization [176]. Other catalysts that facilitate crystallization in silica class are water [177], noble metals [178], and alkali ions [160]. The silica polymorph that forms depends on the crystallization temperature [179]. 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, since incorporation of Li into the amorphous silica results in the highest per-
turbation of the silica framework. Procedures reported in the literature commonly start from glassy silica containing the metal atoms acting as a catalyst, or they require the presence of water or amorphous carbon. It is obvious that the approaches to catalyze the crystallization of silica are not compatible with state of the art silicon technology and clean room standards. We have overcome this problem by a procedure that combines thermal oxidation of silicon with the crystallization of the silica then formed by traces of Li. Here, we take advantage of the volatility of Li at high temperatures. As it is obvious from our results, it is sufficient to locate a Li source inside the furnace used for the oxidation, which is not in direct contact with the sample being oxidized. Evaporated Li is sufficient to promote crystallization in thermal oxide layers grown on a silicon substrate.

6.2.2 Fabrication of crystalline SiO$_2$ microtubes

In this section, we show that traces of evaporated lithium trigger crystallization in silica integrated into common silicon microstructures. The selected crystallization temperature determines which polymorph forms. As described in chapter 3, a large ranges of pore diameters and pore lengths in macroporous silicon are accessible by photolithographically pre-patterned, (100)-oriented n-type silicon wafers. As example in case, we have investigated quartz and cristobalite microtubes obtained from macroporous silicon (Si) with a pore diameter of 1 µm and pore depths ranging from 100 µm to 150 µm. We placed macroporous Si and a crucible containing some lithium niobium isoproxide (LiNb(O$_3$H$_7$)$_5$ wt-% solution Alfa Aesar) in a furnace and heated the samples at a rate of 10°C/min to 1050°C, 1100°C and 1200°C, respectively. Then, the samples kept at these temperatures for 2 hours, and subsequently cooled to room temperature at a rate of 1°C/min. The entire procedure was carried out under ambient conditions.

6.2.3 Morphology of SiO$_2$ microtubes

Figure shows a SEM image of the surface of a macroporous Si membrane annealed at 1050°C. The pore walls are SiO$_2$ microtubes that appear as bright annuli surrounding the pore openings. Apparently, the silica layer has a uniform thickness. We selectively released the SiO$_2$ tubes either partially or completely by etching the residual Si with 30 wt-% aqueous KOH at 80°C. After an etching time of 15 minutes approximately 30 µm of the tubes were released, whereas the lower tube segments were still embedded into the Si matrix (Fig.). After an etching for 90 minutes
the silica tubes are completely liberated. Their high mechanical stability prevents the microtubes from breaking. Fig.1c is a representative SEM image of a single silica microtube with an aspect ratio of 140, corresponding to that of the pores in the macroporous Si that had been oxidized. We note that also in SEM images containing a large number of silica microtubes no short segments of broken tubes are seen (Fig. 6.6c). The walls of the microtubes are smooth and free of defects (Fig. 6.6d). A TEM image of an ultra-thin slice containing a section across a silica microtube is seen in Figure 6.6e (the preparation of ultra-thin slice for TEM investigation were described in section 4.3.4). Its wall broke during the cutting into segments with lengths of 200-500 nm. The wall thickness of around 80-90 nm is in line with the values obtained from the SEM.

6.2.4 X-ray diffraction of SiO\textsubscript{2} microtubes

XRD on ensembles single silica microtubes revealed that all three low-pressure SiO\textsubscript{2} polymorphs, quartz, tridymite and cristobalite, were obtained depending on the crystallization temperature applied. Figure 6.7 shows XRD patterns of the released SiO\textsubscript{2} microtubes, which were deposited on silicon wafers. The samples were crystallized at 1050°C (Fig. 6.7a), 1100°C (Fig. 6.7b) and 1200°C (Fig. 6.7c). A peak centered at 2\(\theta\) = 21.9°, which can be indexed as the (101) reflection of cristobalite (JCPDS: 76-0937), appeared in all three diffraction patterns. In case of the sample crystallized at 1050°C (Fig. 6.7a) strong (100) and (011) peaks of quartz were occur at 2\(\theta\) = 20.8° and 2\(\theta\) = 26.6° (JCPDS: 88-2487). Tridymite (JCPDS: 89-3141) traces were also appeared indicated by the appearance of small peaks at 23.2° (101), 30° (102) and 35.8° (110) in figure 6.7b. The reflection signals of cristobalite increase with increasing of the annealing temperature, for the sample annealed at 1200°C, a pure cristobalite phase was achieved (Fig. 6.7c).

6.2.5 Electron diffraction pattern of SiO\textsubscript{2} microtubes

Different SiO\textsubscript{2} polymorphs were observed by TEM. For the sample with thermal oxidation at 1050°C, quartz (hexagonal; P\texttextsubscript{3}\textsubscript{2}12\textsubscript{1}; zone axis ⟨001⟩) was the dominate phase. Figure 6.8b shows a representative SAED pattern with the Bragg spots corresponding to the (110) and (-210) reflections of hexagonal quartz, indicating the single crystalline nature of the microtubes. Tridymite (hexagonal; P\texttextsubscript{6}3\textsubscript{2}12\textsubscript{1}; zone axis (001)) appeared when increasing the temperature to 1100°C (Fig. 6.8c; d). The Bragg spots, shown in Figure 6.8e, is arise due to (-100) and (2-10) reflections of the hexagonal tridymite. Cristobalite (tetragonal; P\texttextsubscript{4}1\textsubscript{2}1\textsubscript{2}; zone axis ⟨001⟩) was finally
Figure 6.6: Electron Microscopy images of quartz tubes. Samples were prepared by heating the macroporous silicon (pore diameter = 1 µm, pore length= 150 µm) to 1050°C at a rate of 10°C/min, then kept at this temperature for 2h, and cooled to room temperature at a rate of 1°C/min. (a) SEM micrograph of a plan view of quartz tubes regularly embedded in macroporous silicon matrix. (b) Partially liberated quartz tube arrays. (c) Many completely released quartz tubes and (d) an individual tube on a silicon wafer. (e) Ultra thin slice containing a section across a silica tube (preparation of ultra thin slices is described in section 4.3.4).
Crystal modification of SiO$_2$ microtubes was investigated by $\theta$/2$\theta$ scans. XRD results of complete released microtubes on silicon wafer, obtained by thermal oxidation of macroporous Si (Dp = 1 $\mu$m; Lp = 100 $\mu$m) in lithium for 2h at temperature of (a) 1050°C, (b) 1100°C, (c) 1200°C. (\textcolor{red}{$\ast$}: quartz, $\textcolor{red}{\#}$: tridymite, $\textcolor{red}{\#}$: cristobalite).

achieved at 1200°C (Fig. 6.8e, f). The Bragg spots in the SAED pattern shown in Figure 6.8f can be assigned to (-110) and (200) reflections of the tetragonal cristobalite structure. No amorphous silica is present in the tubes subjected to thermal oxidation in the presence of lithium. Under our preparation conditions, we believe the microtubes are first formed in the $\alpha$-form, and are then converted to the $\beta$-form on further heating and cooling to room temperature. The SAED-pattern of SiO$_2$ microtubes at different temperatures reveal that TEM investigations are in good agreement with that of XRD.

6.2.6 SiO$_2$ thin films

In order to demonstrate that lithium actually acted as a catalyst and induced the SiO$_2$ amorphous/crystalline phase transitions, we explored the thermal oxidation of a flat Si wafer. As expected, the thermal oxidation of Si conducted under the same oxidation conditions but in a furnace without Li contaminations exclusively yielded amorphous SiO$_2$. In contrast, a cristobalite thin film was obtained by thermal oxidation of a silicon wafer at 1250°C in the presence of lithium for 2h. Figure 6.9 is the XRD
Figure 6.8: TEM investigation on SiO$_2$ microtubes. The samples were prepared by thermal oxidation of macroporous Si (D$_{p}$= 1 µm, L$_{p}$= 100 µm) at temperatures of 1050°C, 1100°C, 1200°C in the presence of lithium, respectively. (a) Quartz (hexagonal) microtubes obtained at 1050°C. (b) Its selected area electron diffraction pattern (SAED). (c) Tridymite tubes obtained at 1100°C. (d) Its selected area electron diffraction pattern (SAED). (e) Cristobalite (tetragonal) microtubes obtained at 1200°C. (f) Its selected area electron diffraction pattern (SAED) (lattice reflections are indexed).
pattern of a SiO\textsubscript{2} thin film fabricated by annealing the silicon wafer in the presence of lithium at 1250°C. As expected, the pure cristobalite phase was obtained. The peak at 2\(\theta\) = 32.8° is the (200) reflection of Si forbidden peak which only occurs when the Si lattice is distorted. XRD results reveal that the effect of the temperature on the phase transition does not follow exactly the thermodynamic stability order of the pure silica phases.

![Figure 6.9: XRD pattern of SiO\textsubscript{2} thin film obtained by annealing Si wafer in present of lithium at 1250°C for 2h (*: Si(200)).](image)

TEM images of SiO\textsubscript{2} thin film cross sections are shown in Figure 6.10 (the cross section X-TEM specimen preparation procedure is discussed in section 4.3.4). The thin film has a thickness of around 800 nm. The bright field image (Fig. 6.10a) together with the corresponding dark field (Fig. 6.10b) image indicates that the thin film has single-crystalline segments extending several square micrometers. The occurrence of spots in a typical SAED in Figure 6.10c can be assigned to the (111), (0-11) of cristobalite (tetragonal, P4\(_1\)2\(_1\)2\(_1\)). Energy dispersive X-ray analysis (EDX) proves stoichiometric SiO\textsubscript{2} tubes were obtained. The features of the electron energy loss spectroscopy (EELS) spectrum coincides with that of a standard SiO\(_2\) (Fig. 6.10d).

In summary, SiO\textsubscript{2} crystalline microtubes with a pore diameter of 1 \(\mu\)m, and pore lengths from 100 to 150 \(\mu\)m were fabricated by thermal oxidation of macroporous silicon in the presence of lithium. All the three SiO\textsubscript{2} low pressure phases, quartz, tridymite, and cristobalite, were obtained by varying the annealing temperature from 1050°C to 1200°C. In addition, a highly crystalline SiO\textsubscript{2} thin films were obtained by annealing the Si wafer in lithium at 1250°C for 2h. We believe that the study of lithium-induced crystallization in amorphous SiO\textsubscript{2} microtubes is of high significance because it demonstrates a novel and simple approach to fabricate crystalline SiO\textsubscript{2} nano- and microstructures.
Figure 6.10: TEM cross section investigations on SiO$_2$ (cristobalite) thin film. Sample are prepared by heating Si wafer in lithium to 1250°C at a rate of 10°C/min, kept at this temperature for 2 hours, and cooled to room temperature at a rate of 1°C/min. (a) Bright field. (b) Dark field image. (c) A typical selected area electron diffraction pattern (SAED image). (d) EELS of the thin film, measured at the location indicated in (a).
6.3 Summary of the chapter

Modification of macroporous silicon by microtubes, either LiNbO$_3$ and Er:LiNbO$_3$ or crystalline SiO$_2$ microtubes was discussed in the chapter. LiNbO$_3$ and Er:LiNbO$_3$ microtubes were prepared by a modified templated high-temperature conversion approach, so-called high temperature melt wetting. Crystalline SiO$_2$ microtubes were fabricated by crystallization of thermally grown amorphous SiO$_2$ tubes in macroporous silicon templates in the presence of trace amount of lithium.