

Video Article

Preparation of Macroporous Epitaxial Quartz Films on Silicon by Chemical Solution Deposition

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Abstract

This work describes the detailed protocol for preparing piezoelectric macroporous epitaxial quartz films on silicon(100) substrates. This is a three-step process based on the preparation of a sol in a one-pot synthesis which is followed by the deposition of a gel film on Si(100) substrates by evaporation induced self-assembly using the dip-coating technique and ends with a thermal treatment of the material to induce the gel crystallization and the growth of the quartz film. The formation of a silica gel is based on the reaction of a tetraethyl orthosilicate and water, catalyzed by HCl, in ethanol. However, the solution contains two additional components that are essential for preparing mesoporous epitaxial quartz films from these silica gels dip-coated on Si. Alkaline earth ions, like Sr²⁺ act as glass melting agents that facilitate the crystallization of silica and in combination with cetyl trimethylammonium bromide (CTAB) amphiphilic template form a phase separation responsible of the macroporosity of the films. The good matching between the quartz and silicon cell parameters is also essential in the stabilization of quartz over other SiO₂ polymorphs and is at the origin of the epitaxial growth.

Video Link

The video component of this article can be found at <http://www.jove.com/video/53543/>

Introduction

When a piezoelectric material like α -quartz is submitted to a voltage bias it undergoes a mechanical deformation. If this material is porous, these volume changes can lead to pore expansion or contraction, creating a responsive system similar to what may be observed in living biological organelles.¹ Deformable porous α -quartz has been produced using microfabrication,² but such techniques cannot yet produce 3-D pore structures, and pore diameters are on the order of hundreds of nanometers. Crystallization of structured amorphous silica has been hindered by inhomogeneous nucleation caused by high surface energies and architectural deformation due to coarsening and melting. Moreover, since all forms of silica are built upon extremely stable SiO₄ tetrahedral networks, the free energies of formation of amorphous silica, α -quartz and other SiO₂ polymorphs are nearly equal in a wide range of temperatures, making it difficult to produce α -quartz as a single polymorph from the crystallization of an amorphous silica gel.³ Another aspect that makes harder the controlled crystallization of structured amorphous silica is that quartz presents a relatively slow nucleation rate but an extremely fast growth rate, reported between 10-94 nm/sec.^{4,5} Slow nucleation coupled with fast growth tends to generate crystals much larger than the original nanoporous structure, thus the original morphology is lost. Alkali metals, such as Na⁺ and Li⁺, have been used to crystallize α -quartz, frequently in combination with hydrothermal treatment.^{5,6} Also, a Ti⁴⁺/Ca²⁺ combination was employed to crystallize spherical particles of silica into quartz by a soft chemistry route using silicon alcoxides.⁷ However, the controlled crystallization of a structured amorphous silica film into quartz remained a challenge.

Recently, strontium has been found to catalyze the nucleation and growth of crystalline SiO₂ under ambient pressure and relatively low temperatures.^{8,9} Epitaxy, arises from the favorable mismatch between α -quartz and the <100> silicon substrate, producing oriented piezoelectric thin films. Evaporation-induced self-assembly to produce mesoporous silica films has been used since 1999.¹⁰ This technique has been studied and applied to a multitude of templating agents under various conditions to produce pores of variable sizes and mesophases. It has been found that subnanometric changes in mesopore size can have a dramatic effect on solute diffusion through porous systems¹¹, validating this extensive attention to pore structure. Moreover, accessibility to the internal silica pore system can be obtained by controlling the micellar phase of the template.¹²

Here, the synthesis route that allows unprecedented control over the thickness and pore size of amorphous silica layers using a novel phase separation is demonstrated.¹³ These films are infiltrated with Sr(II) salts and crystallized to α -quartz at 1,000 °C under air at ambient pressure. The pore size retainable using this crystallization process is determined, and the effect of wall thickness and film thickness is studied. Finally the piezoelectricity and the deformability of the pore system are studied.

Protocol

1. Preparation of the Sol

1. Prepare a solution of prehydrolyzed tetraethyl orthosilicate (TEOS) the day before the preparation of the gel films in a fume hood in which a lab balance and a magnetic stirrer are placed. In this step and throughout the protocol wear a lab coat, gloves and safety goggles.
 1. In a 50 ml beaker containing a Teflon coated magnetic stirring bar weigh 1.68 g of CTAB, add 48.13 ml of ethanol and 3.00 ml of HCl 35%, cover the beaker with a watch glass and stir until the CTAB is completely dissolved.
 2. Add 7.37 ml of TEOS to the beaker dropwise (at a rate of about 1-2 drops per second) while stirring, cover the flask with a watch glass and let it stir O/N.
2. The next day, prepare a 1 M aqueous solution of Sr^{2+} . Perform this and the following steps just before the preparation of the gel films because an aged solution is prone to re-precipitation of the Sr salt.
 1. Weigh 6.6654 g of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ into a 25 ml volumetric flask.
 2. Add ultrapure water (e.g., Milli-Q) up to 25 ml (meniscus tangent to the flask mark) and close the flask with a plastic cap and gently shake the flask to dissolve the strontium chloride.
3. Add 2 ml of the 1 M aqueous solution of Sr^{2+} to the 50 ml glass beaker containing the sol that was left stirring O/N. Stir the solution for 25 min.
4. Dispose the residues that have been eventually generated according to the safety and environment protection protocols of the lab.

2. Gel Film Deposition on Si(100) Substrates

1. Preparation of the substrates
 1. Cut Si slabs of about 2 cm by 5 cm out of a 2-inch p-type (100) silicon wafer with a thickness of 200 micron by cleaving the wafer in a direction parallel or perpendicular to the wafer flat using a diamond tip or a sharp-edged object. Perform this step in advance, for instance the day before the deposition of the gel films.
 2. Just before the deposition of the gels, clean the substrates with ethanol and let them dry or use a nitrogen flow or compressed air to accelerate the drying. Perform this step while waiting for the completion of step 1.3.
2. Coat the films. In order to obtain a homogeneous macropore structure perform this step under conditions of relative humidity between 20% and 55% at RT.
 1. Establish a dip coating sequence. Select the initial and final positions taking into account the actual length of the Si slab and the level of the solution in the beaker so that the slab is at least 2 cm above the solution level at the starting position and 1 cm above the bottom of the beaker at the end of the immersion. Set both the immersion and withdrawal speeds to 150 mm/min. Set the immersion time (time at the final position) to zero.
 2. Upon completion of step 1.3 place the beaker with the solution in a well-centered position beneath the Si slab hanging from the dip-coater arm.
 3. Fix one end of the Si slab to the dip-coater arm with the clip, ensuring the slab is as perpendicular as possible with respect to the horizontal.
 4. Execute the dip coating sequence and unclip the Si slab from the dip-coater arm. Repeat steps 2.2.3 and 2.2.4 with additional Si slabs to produce more films, taking care not to extend these preparations beyond 1 hr, to ensure that the stability of the solution is not compromised.
3. Dispose the solutions that have been eventually generated according to the safety and environment protection protocols of the lab.

3. Gel Film Crystallization by Thermal Treatment

1. Thermal treatment of the gel films on Si(100).
 1. Program a furnace to perform the following thermal treatment in air atmosphere: heating from RT to 1,000 °C at 3 °C/min, holding at 1,000 °C for 5 hr and cooling to RT at 3 °C/min.
 2. Place the dip-coated Si substrates in an alumina boat, introduce it in the furnace and execute the thermal treatment.
2. Cleaning of the crystallized films.
 1. Immerse the crystallized films for 3 hr in concentrated HNO_3 in order to remove the accumulations of Sr^{2+} that have been expelled to the film surface during the crystallization and then rinse the films first with deionized water and then with ethanol.

Representative Results

The progress of the material synthesis was controlled by monitoring different aspects. After the dip-coating process one can observe the aspect of the films, the eventual appearance of diffraction structures in the reflected spot of a green laser and the Scanning Electron Microscopy (SEM) images in backscattered electrons mode (**Figure 1A-B**). After the crystallization process it is important to record Atomic Force Microscopy (AFM) topographic images (**Figure 1C**) and a pole figure obtained by X-ray diffraction of the films that indicates that the epitaxial relationships between the α -quartz film (α -Q) and the Si(100) substrate are: α -Q(010)//Si(010) and α -Q(001)//Si(001) (**Figure 1D**). The piezoelectric response of the films is detected by the converse piezoelectric effect using an atomic force microscope with a conducting tip in contact mode and applied AC voltages between the tip and the Si(100) substrate (**Figure 2**).

During the preparation of the material there are several measurements and observations that can be made to check the progress of the synthesis. These are represented in **Figure 1**, along with a sketch that displays the different stages of the material preparation. After the deposition of the film by dip-coating, the bluish-greenish appearance that can be appreciated by the naked eye observation of the substrate (**Figure 1A**) is indicative of a good distribution of Sr^{2+} all over the film. Also at this stage one can direct a green laser to the film and intercept the reflected spot in a black screen. If the phase separation has occurred and presents a periodicity close to that of the laser wavelength ($\lambda = 532 \text{ nm}$) diffraction spots can be observed (inset of **Figure 1A**). A straightforward examination of the material that reveals the occurrence of the phase separation resulting in a macropore structure (with diameter between 0.5 and 1 micron) and a Sr^{2+} distribution at the edge of the macropores can be done by scanning electron microscopy in backscattered electrons mode (see **Figure 1B**).

Concerning the outcome of the thermal treatment of crystallization there are two measurements to assess the quality of the final material. On the one hand, using atomic force microscopy in tapping mode, the topographic images reveal to what extent the initial macroporous structure has been preserved upon crystallization (**Figure 1C**). On the other hand, the acquisition of an X-ray diffraction pattern with an area detector immediately reveals if an epitaxial quartz film (diffraction spots are observed instead of rings) with the α -quartz(100) texture out of plane has been obtained, as only the (h00) family of reflections is observed in a θ - 2θ scan (see **Figure 1D**).

Piezoresponse force microscopy can be used to check that the crystallized films present a piezoelectric response via the converse piezoelectric effect. This is done by applying an AC voltage between a conducting AFM tip and the Si(100) substrate and bringing the tip in contact with the film surface in static conditions. The amplitude of deflection of the tip is recorded while performing a frequency scan of the AC voltage applied between the tip and the substrate. If the film is piezoelectric it deforms under the applied voltage and this can be detected through the deflection of the tip at a particular resonance frequency (see **Figure 2**). This deflection amplitude is proportional to the amplitude of the applied AC field (see inset of **Figure 2**). A piezoelectric strain coefficient can be obtained from these measurements which for the orientation of these quartz films is of the order of 2 pm/V , in agreement with the values of bulk quartz.

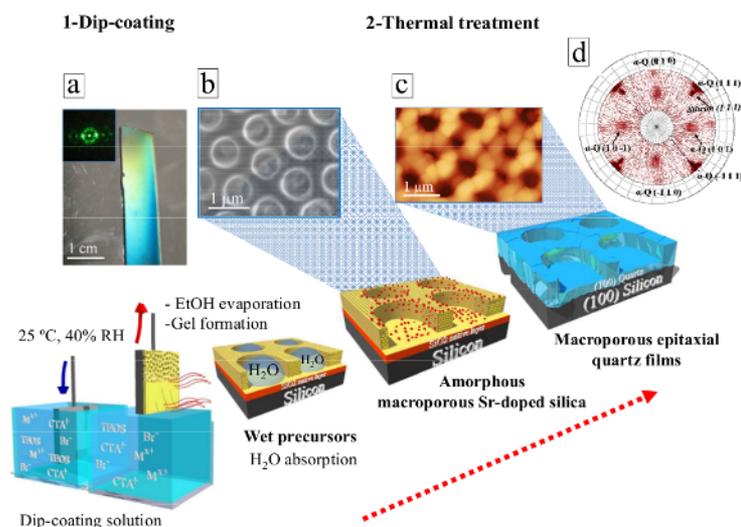


Figure 1. Material preparation and characterization. Different stages of the preparation of macroporous epitaxial quartz films on (100)Si together with the different characterizations to monitor the progress of the process: **(A)** Optical image of the gel film on (100)Si after dip coating. The inset shows the diffraction spots produced by the interaction of the macropores with a green laser. **(B)** SEM image of the gel film on (100)Si after dip coating in the backscattered electrons mode. The increased with contrast at the edges of the macropores is due to the accumulation of Sr^{2+} . **(C)** Topographic AFM image of the film after the crystallization process that the macroporous structure has been preserved and showing crystals surrounding the macropores. **(D)** X-ray diffraction pattern recorded in a 2-dimensional detector showing the spot-like (100) and (200) reflections of α -quartz. [Please click here to view a larger version of this figure.](#)

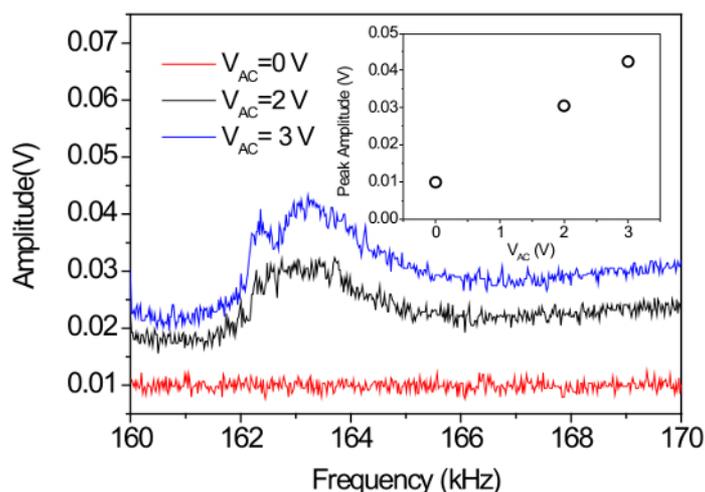


Figure 2. Piezoelectric response of the films. The piezoelectric response of the crystallized quartz films is checked by detecting the deflection of a conducting AFM in contact with the film while Alternating Current (AC) voltages of different frequencies are applied between the tip and the Si(100) substrate. The inset shows that as expected for the piezoelectric response the deflection amplitude varies linearly with the amplitude of the applied AC voltage. [Please click here to view a larger version of this figure.](#)

Discussion

The presented method is a bottom-up approach to produce macroporous quartz films on Si. Compared to the standard method of production of quartz films, a top down technology based on cutting and polishing of large hydrothermally grown crystals, the method described in the protocol allows obtaining much thinner films with thicknesses between 150 and 450 nm which can be controlled with the withdrawal rate. All experimental details regarding the control of quartz films thickness, and piezoelectric response are reported in references^{8,13}. The thicknesses of the quartz films obtained by standard method cannot be below 10 μm and for most applications these need to be bonded on Si substrates.

The quartz films obtained with the protocol could find applications in the future in the field of electromechanical devices. Due to its thicknesses below 500 nm these are expected to present higher resonance frequencies. A key aspect in order to obtain films of good quality is ensuring that the length of the Si substrate is long enough, typically more than 4 cm long, in order to allow the formation of the meniscus between the surface of the sol and the substrate that is being pulled out. At the final stage of the dip-coating process the meniscus (typically of 1 cm length) is located at the bottom end of the substrate. As a result, the film presents a non-uniform thickness in this part which has to be removed by cutting it out before the thermal treatment. This is done to ensure that the piezoelectric response is homogeneous since the remaining part of the film presents a homogeneous thickness.

The method has some limitations. For instance, the formation of macroporosity within the range of 500 nm and 600 nm only occurs when relative humidity is between 20% and 55% and is also optimized for a relatively narrow range of temperatures (typically between 15 and 35 °C). This protocol is specifically related to the synthesis of epitaxial quartz films with macroporous within the range of 500 nm and 600 nm diameter. The size of this macroporosity cannot be modified due to the phase separation mechanism. However the thickness of the film can be controlled and all these experimental details are properly reported elsewhere.^{8,13} Also, the thickness of the film is not perfectly uniform and increases at the bottom of the film, *i.e.*, the last part that is in contact with the sol during the withdrawal. However this limitation can be easily overcome by cutting off and discarding this part of the film with non-uniform thickness.

Disclosures

The authors have nothing to disclose.

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