

# Chiral habit selection on nanostructured epitaxial quartz films.

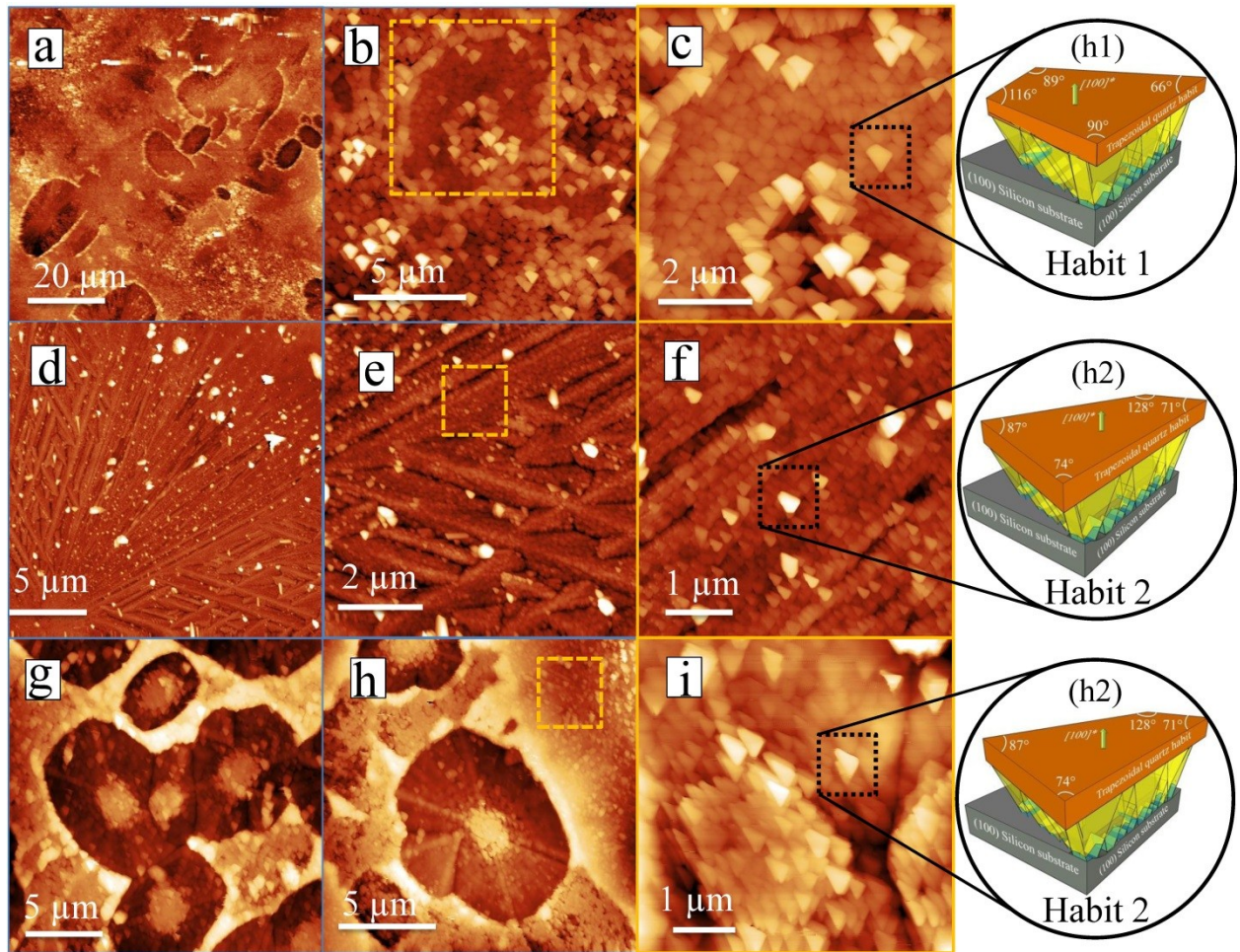
Adrián Carretero-Genevri, Martí Gich, Laura Picas, Clément Sanchez, Juan Rodriguez-Carvajal

## Experimental Procedures and Materials

*Materials.* All chemicals were obtained from Aldrich and used as received. Films structure was investigated using a field emission gun scanning electron microscope (FEG-SEM), Hitachi's SU77. Quartz habit morphology was investigated using an AFM multimode-V microscope controlled by Nanoscope-V electronics and the Nanoscope 8 software (Bruker AXS Corporation, Santa Barbara, CA). V-shaped Si<sub>3</sub>N<sub>4</sub> cantilevers (SNL, Bruker AXS Corporation, Santa Barbara, CA) with a nominal spring constant of 0.35 N/m, nominal resonant frequency of 65 kHz and a nominal tip radius of 3 nm were operated under air.

### *Experimental details.*

Synthesis of dense quartz films: Mesoporous silica films were prepared from solutions composed of TEOS:Brij-56:H<sub>2</sub>O:EtOH:HCl with a molar ratio of 1:0.05:5:25:0.7. TEOS was first dissolved in a solution containing EtOH, 2 M HCl and H<sub>2</sub>O before adding Brij-56. The resulting solution was stirred for at least 2 h before deposition on silicon substrates by dip-coating at room temperature under 40% relative humidity. The thickness of the silica was tuned by using different dipping rates (1, 2, and 4 mm·s<sup>-1</sup>) while keeping the other dip-coating conditions constant. After coating, films were immediately thermally treated at 450 °C for 10 min in air. Once the amorphous silica was fabricated, either a 1 M Sr(NO<sub>3</sub>)<sub>2</sub> or a 1 M Ba(OH)<sub>2</sub> solution was infiltrated into the SiO<sub>2</sub> layer using dip-coating (dipping rates 2 mm·s<sup>-1</sup>), and then the excess catalyst was removed from the silica surface by carefully wiping the film. A thermal treatment of 1000 °C for 5 h (ramp temperature 3 °C/min) under oxygen atmosphere was performed directly after dip-coating in a furnace in order to obtain dense quartz films.



**Figure S1.** AFM topography images supporting other examples performed on quartz films surface, confirming the existence of only one of these two distinct habits, i.e. h1 and h2.

### Morphological calculations from AFM images

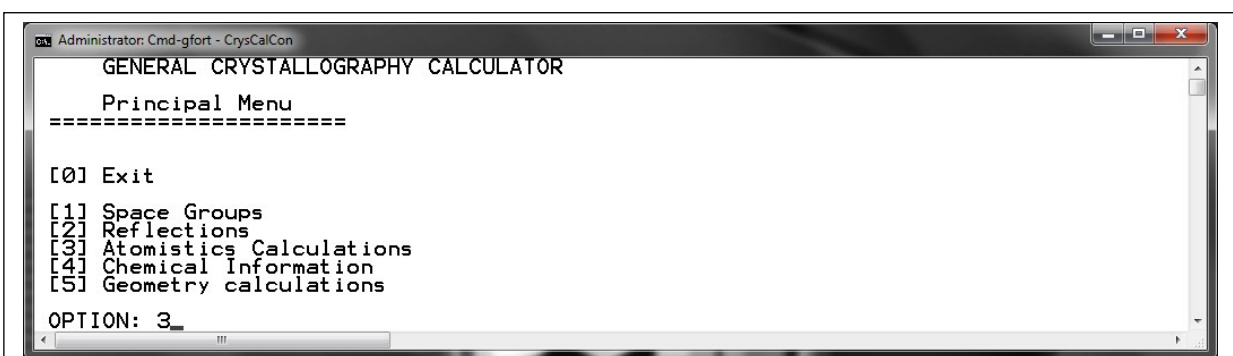
The AFM images show two kinds of habits of alpha-quartz crystallites. The observed top surface corresponds always to the (100) planes of quartz as shown by X-ray diffraction. The surface is limited by four edges so that they are shown as trapezoids with well-defined angles.

In order to get the maximum information from the geometry of observed crystallites in AFM images, few modules were introduced in the console crystallographic calculator program (**CrysCalCon**) existing in the CrysFML repository (see reference 10 of the manuscript). The details of the calculations may be consulted in the source code (in particular the module menu\_5.f90) of the program that is available at: [http://forge.epn-campus.eu/projects/crysfml/repository/show/Program\\_Examples/Cryst\\_calculator\\_console](http://forge.epn-campus.eu/projects/crysfml/repository/show/Program_Examples/Cryst_calculator_console)

The aim of the calculations was to obtain what are the most probable indices of the trapezoids observed edges as well as the possible planes intersecting the (100) at the different edges. This last item, lateral planes, provides information on possible full polyhedral shapes of crystallites. The lateral planes are not visible in AFM images. We assume that we have to select always the lowest indices compatible with the observations.

The observations consist on the fact that we are concerned with the (100) plane and three of the four internal angles of the trapezoids (the sum is always equal to 360 degrees). We estimate about 4° the maximum error in the measurement of angles.

For running the program one needs only to know the unit cell of the compound and the experimental information. When the program is invoked in a console terminal one gets the

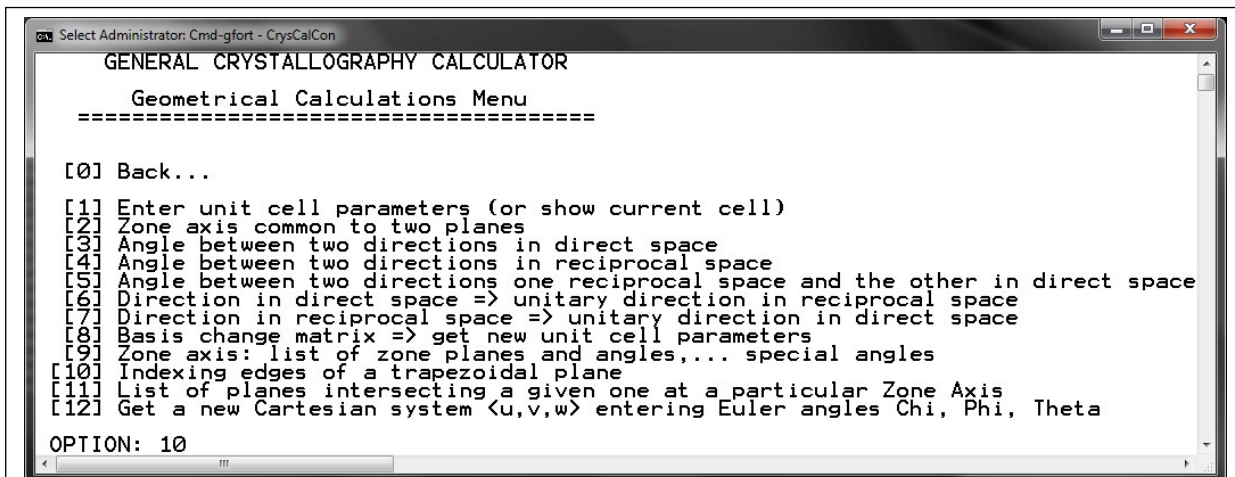


```
Administrator: Cmd-gfort - CrysCalCon
GENERAL CRYSTALLOGRAPHY CALCULATOR
Principal Menu
=====
[0] Exit
[1] Space Groups
[2] Reflections
[3] Atomistics Calculations
[4] Chemical Information
[5] Geometry calculations
OPTION: 3_
```

**Figure S2:** Main menu of the program **CrysCalCon**. For our purposes we need to select the option [3] in order to load a CIF file with the structural information.

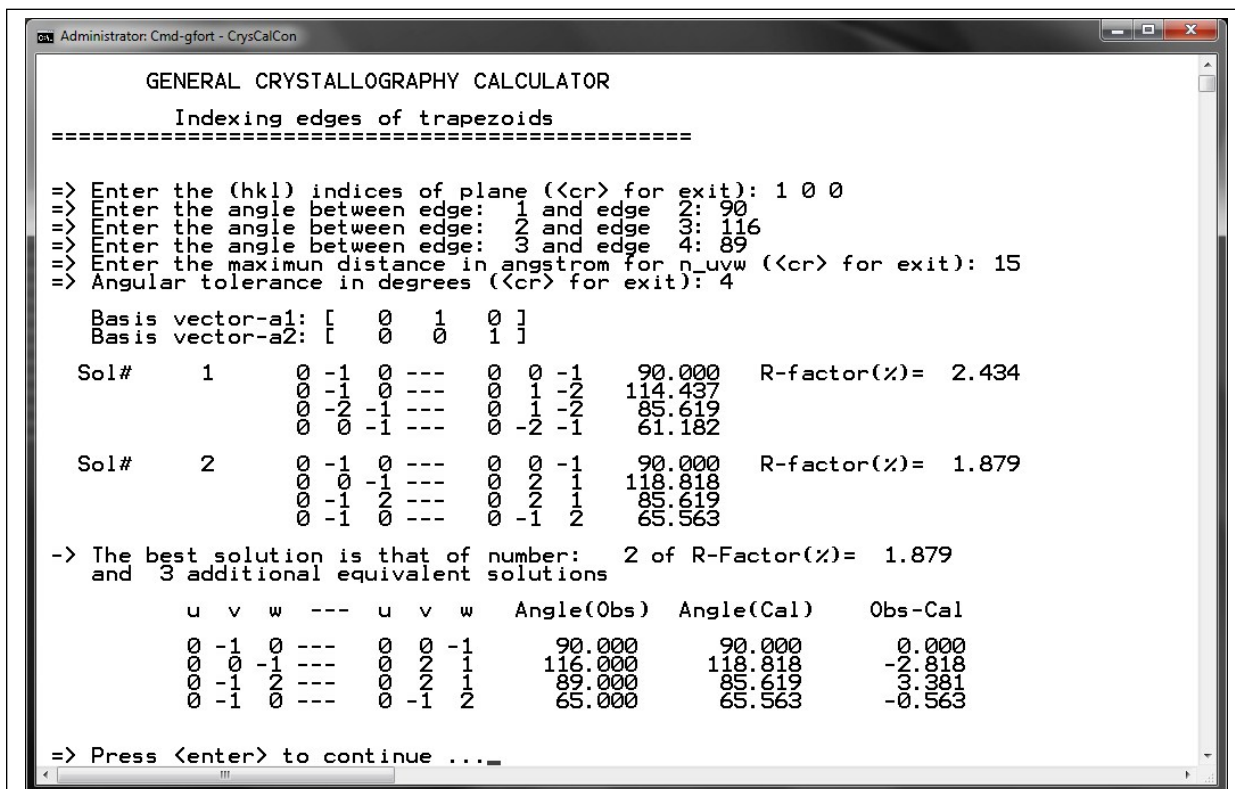
following:

After reading the CIF file corresponding to alpha-quartz (we used the ICSD database code 90145) with unit cell parameters  $a = 4.9158(10) \text{ \AA}$  and  $c = 5.4091(18) \text{ \AA}$ , we have to select option [5] (see Figure S1) to perform the geometrical calculations. One obtains the following panel:



**Figure S3:** Geometrical calculations menu of the program **CrysCalCon**. Selecting the option [10] we enter in the indexing edges of trapezoidal planes.

Entering option [10] we need to provide the indices of the trapezoidal plane (in our case 1 0 0), the list of three observed angles, the maximum module ( $n_{uvw}$  in Angstroms) of crystallographic



**Figure S4:** Option [10] of the geometrical calculations menu of the program **CrysCalCon**.

directions representing the edges and the angular tolerance in degrees. A value of  $n_{uvw}$  is needed

in order to limit the solutions to those having reasonable small indices. An example, corresponding to habit h1 in the main text, is given in Figure S3.

Once we have the solution provided by this part of the program we can go to option [11] of the geometrical calculation menu of **CrysCalCon** in order to get the list of possible lateral angles for each edge of the trapezoid. These are planes belonging to the zone axes represented by the indices of the edges. We present an example in the following panel:

```

Administrator: Cmd-gfort - CrysCalCon

GENERAL CRYSTALLOGRAPHY CALCULATOR

List of planes intersecting a given one at a particular Zone Axis
Forming an angle with the given plane within the interval [ang1,ang2]
=====
=> Enter the (hkl) indices of the Plane (<cr> for exit): 1 0 0
=> Enter the [uvw] indices of the Zone Axis (<cr> for exit): 0 1 -2
=> Enter the angular range to consider (<cr> for exit): 60 100
=> Enter the minimum d-spacing of planes (<cr> for exit): 1

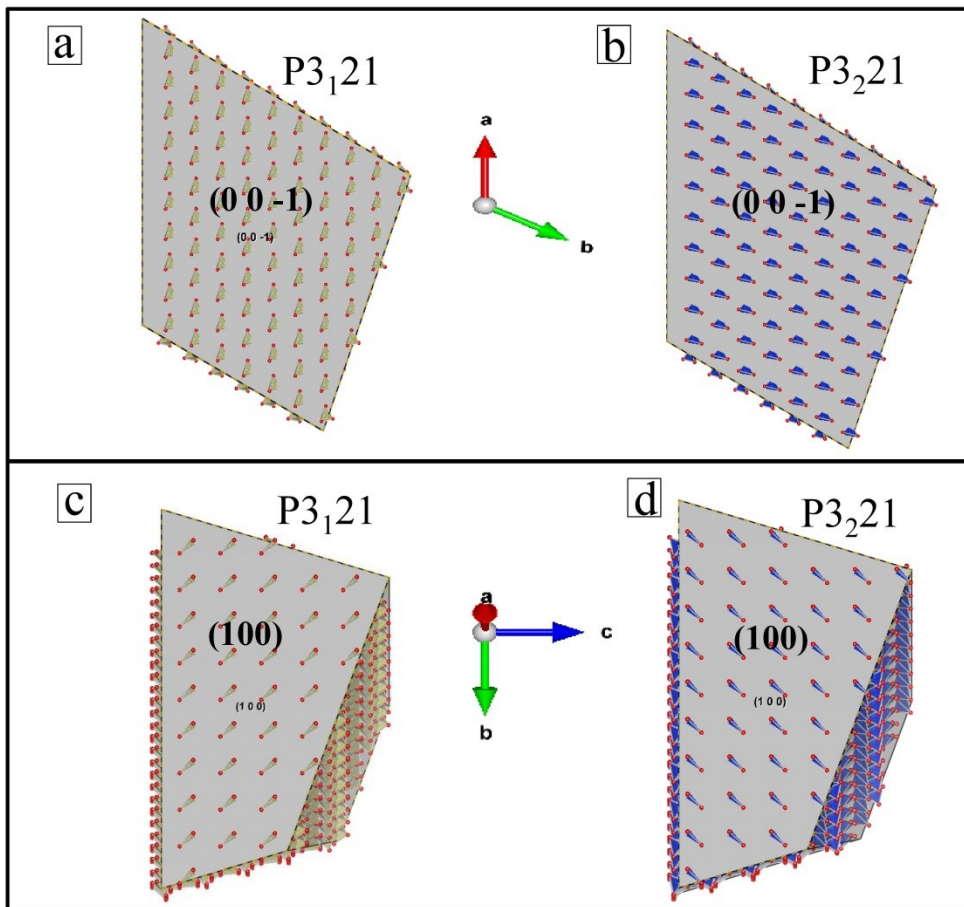
=> List of planes intersecting ( 1 0 0) at the zone axis: [ 0 1 -2]
# 1 (hkl): 0 -2 -1 Angle: 62.272 degrees
# 2 (hkl): 1 -2 -1 Angle: 90.000 degrees
# 3 (hkl): 1 -4 -2 Angle: 75.275 degrees
# 4 (hkl): 1 -6 -3 Angle: 70.689 degrees
# 5 (hkl): 2 -6 -3 Angle: 80.062 degrees
# 6 (hkl): 4 -6 -3 Angle: 99.938 degrees

=> Press <enter> to continue ...
  
```

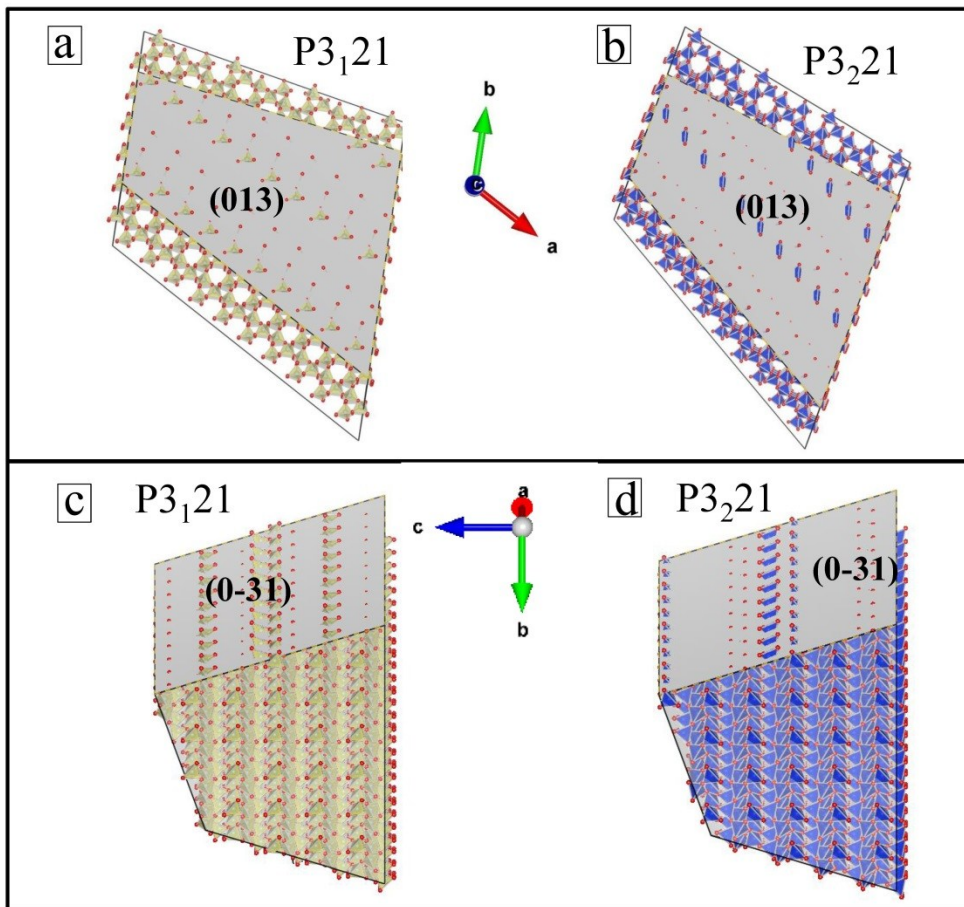
**Figure S5:** Calculations of possible lateral planes corresponding to the option [11] of the geometrical calculations menu.

In Figure S4 we show the list of calculated possible lateral planes intercepting the observed top plane (100) in the AFM images at the edge [01 -2]. We need a minimum d-spacing for the planes in order to limit the values of (*hkl*) indices.

Proceeding as shown above for all the observed edges of both habits we arrive to the selection of limiting planes considered in the main text. Using the program VESTA (see reference 14 of the manuscript) we can construct polyhedral shapes and embed the atomic structure of the two enantiomers of alpha-quartz within the polyhedron and investigate the atomic surfaces. In Fig. S6 we can see that the P<sub>3</sub>121 and P<sub>3</sub>21 enantiomorphs do not present differences in the density of oxygen atoms for the (100) and (00-1) surfaces. In Fig. S7 we can observe that such differences exist for the (013) and (0-31) surfaces.



**Figure S6.** Representation of the (00-1) and (100) surfaces of habit h1 superimposed on their structural model in  $P3_121$  or  $P3_221$  space groups. Notice that these surfaces are equally energetic.



**Figure S7.** Representation of the (013) and (0-31) surfaces of habit h1 superimposed on their structural model in  $P3_121$  or  $P3_221$  space groups. Notice that the surface energy of the planes (013) and (0-31) is about 20% and 7%, respectively.