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Chiral habit selection on nanostructured epitaxial quartz films.

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Understanding the crystallization of enantiomorphically pure systems can be relevant to diverse fields such as the study of the origins of life or the purification of racemates. Here we report on polycrystalline epitaxial thin films of quartz on Si substrates displaying two distinct types of chiral habits that never coexist in the same film. We combine Atomic Force Microscopy (AFM) analysis and computer-assisted crystallographic calculations to make a detailed study of these habits of quartz. By estimating the surface energies of the observed crystallites we argue that the films are enantiomorphically pure and we briefly outline a possible mechanism to explain the habit and chiral selection in this system.

Chiral objects, defined by the lack of mirror plane or center of symmetry, are ubiquitous in nature from molecules to galaxies[1]. The term chiral comes from the Greek, meaning "hand" as this is the prototypical example of chiral object: the mirror image of a right hand is not the same right hand but a left hand. The pairs of objects which as our hands are identical except for its opposite orientations are named enantiomorphs (enantiomers in the case of molecules) and chiral molecules and crystals typically exist in two forms only distinguishable by its contrasting optical activity consisting in rotating the plane-polarized light by an equal amount but in opposite directions. For instance, two forms of quartz (α-SiO$_2$) are found in the lithosphere, levorotatory crystals (L-quartz, space group P3$_1$21) containing right handed helices of SiO$_4$ tetrahedra along its trigonal c-axis and the dextrorotatory enantiomorph (D-quartz space group P3$_2$21) displaying left-handed helices. Natural quartz occurrences are racemic, i.e. the ratio of right and left enantiomorphs is 50:50[2]. The occurrence of racemates is pervasive in the supramolecular and molecular scales, with the notable exception of biomolecules. Indeed, cells only produce levorotatory aminoacids and dextrorotatory sugars. The striking homochirality of living matter is still not understood, most likely because it is connected to the origins of life.[3] It is believed that homochirality might have originated from a mechanism yielding enantiomeric excesses further amplified to attain pure chirality[4] but this remains an open question. Among the

different mechanisms to produce enantiomeric excesses[5], the asymmetric adsorption of one enantiomer on quartz surfaces was demonstrated to account for a significant degree of selectivity[6] but it is compromised by the random handedness of natural quartz.

In this context, it is relevant considering if a system of chirally pure crystals can emerge from an enantiomorphic mixture and studying the mechanisms governing such a process. Interestingly, Viedma has quite recently shown how a racemic population of crystals can achieve a complete chiral purity in a process made possible by the combination of an autocatalytic secondary nucleation and a dissolution-recrystallization[7].

Here we report on the spontaneous selection of one among two distinct variants of the crystalline habit in thin polycrystalline quartz films epitaxially grown on silicon substrates. We argue that the surface energy of each crystalline habit variant is minimized by one of the two enantiomorphs and that the films are expected to be homochiral. Since both quartz enantiomorphs are expected to nucleate with the same probability on (100)-Si surfaces, our purpose is also discussing what mechanisms allow obtaining chirally pure film surfaces in this system.

We prepared dense polycrystalline epitaxial films of α-quartz on (100)-Si substrates by the thermal devitrification of mesoporous amorphous silica films infiltrated with strontium, barium, or calcium catalysts[8, 9]. The amorphous silica films were dip-coated in a water-ethanolic solution of a Si-alkoxide containing CTAB surfactant that allowed obtaining a hexagonal mesoporous structure with 5 nm pore size. Once the crystallization of this silica matrix occurs after thermal treatment at 900 ºC, the porosity of the film collapses, yielding a dense quartz film[8]. X-ray diffraction (XRD) studies of the films revealed an epitaxial growth, with the (100) quartz planes parallel to the (100)-Si substrate and the [210] axis being the crystal growth direction (*i.e.* [100]*, in the reciprocal space)[8].

The main findings of the present work arise from the comprehensive analysis of the surfaces of different film samples by Atomic Force Microscopy (AFM). Fig.1 presents AFM images of two different quartz films (panel a-d and e-h, respectively). In Figs. 1a and 1e we can see the topography of large areas from these films.

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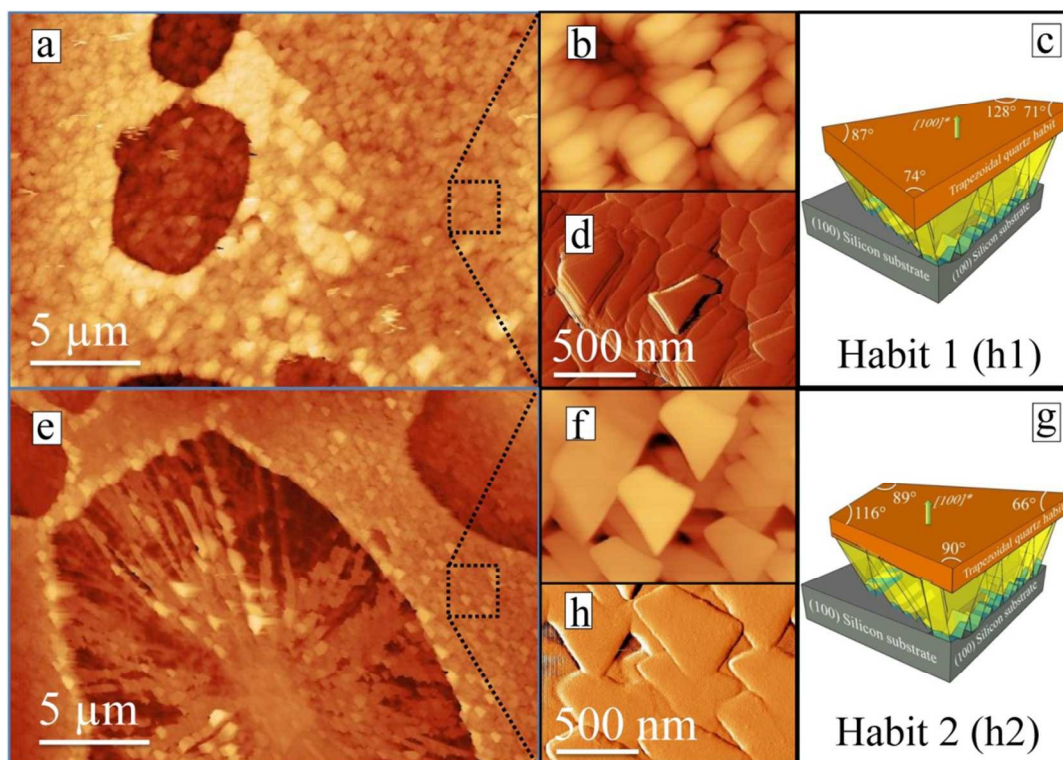RSC**Publishing**

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Fig. 1 AFM topographical and phase images of polycrystalline quartz films surface displaying both h1 and h2 habits (a, b, d and e, f, h, respectively). 3D schematic representation showing the angles (c and g, respectively) extracted from the AFM phase images for the h1 and h2 habits (d and h, respectively).

Detailed scans within these zones indicated by the dashed squares (Figs. 1b, 1f) reveal that both films are polycrystalline and present a dense arrangement of crystals with its upper faces displaying tetragonal irregular convex shapes below 500 nm in size. The study of more than 10 films prepared by the same approach invariably lead us to observe in a given film only one (see figure S1) of the two distinct crystalline habits sketched in Figs. 1c and 1g, hereafter labelled h1 and h2. Moreover, we found that roughly one half of the studied films presented h1 and the other half to h2. Considering the equiprobable appearance of both habits and that only one type of habit can be found in different zones the same film, it is reasonable to assume that some mechanism of habit selection is at play during the crystallisation and growth of the films.

From images of the AFM phase as the ones displayed in Figs. 1g and 1h we made detailed measurements of the inner angles defined by the edges of the top tetragonal faces of h1 and h2, which are reported in the sketches of Figs. 1c and 1g and in Table 1.

In order to get more insight on the crystalline habits of these quartz films we calculated the different habit solutions compatible with the experimental observation of a (100) out of plane texture and a top face characterized by the four inner angles experimentally measured from the AFM images. This was achieved by writing a simple module in the general crystallographic calculator (CrysCalCon)

based on the CrysFML library[10] which selects the lowest index pairs of edges $[uvw]_1$ and $[uvw]_2$ being both perpendicular to [100]* and forming angles close to those experimentally observed (see supporting information figures S2-5 for details).

Experimental angle-h1	Theoretical angle-h1	Crystallographic directions-h1	Planes-h1
87°	86.959°	[0-31]∧[013]	(-131)
128°	126.977°	[0-31]∧[01-3]	(0-1-3)
71°	73.032°	[01-3]∧[010]	(0-3-1)
74°	73.032°	[013]∧[010]	(001)
Experimental angle-h2	**Theoretical angle-h2**	**Crystallographic directions-h2**	**Planes-h2**
90°	90°	[01-2]∧[010]	(001)
116°	118.644°	[010]∧[001]	(010)
89°	85.949°	[0-2-1]∧[001]	(012)
66°	65.407°	[01-2]∧[0-2-1]	(0-2-1)

Table 1. List of calculated possible lateral planes intercepting the observed top plane (100) in the AFM images at the edge [01 -2] for both, h1 and h2 habits of quartz films.

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These calculations indicated the existence of trapezoidal habit solutions presenting inner angles in remarkable good agreement with those obtained by AFM for both h1 and h2 (see second column in Table 1). Notably, the calculations also allowed obtaining the crystallographic planes corresponding to the lateral facets of the crystallites, which could not be imaged by AFM, and its inclination with respect to the substrate plane. Fig. 2 summarizes the orientations of the edges (in red) and the indices of the lateral planes and its orientation with respect to the substrate plane (in blue).
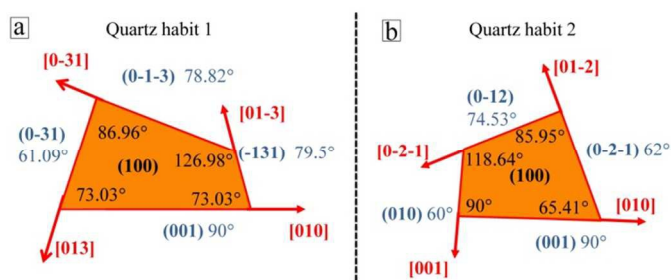

Fig. 2 Habit reconstruction from AFM images (in red, orientations of the edges and in blue, its orientation with respect to the substrate plane).

An additional solution presenting low index lateral faces at 90º with respect to the substrate was found to be compatible with h1 and h2. This was however disregarded because we observed lateral faces at about 60º with respect to the substrate in a scanning electron microscopy study of a film cross section (see Fig. 3).
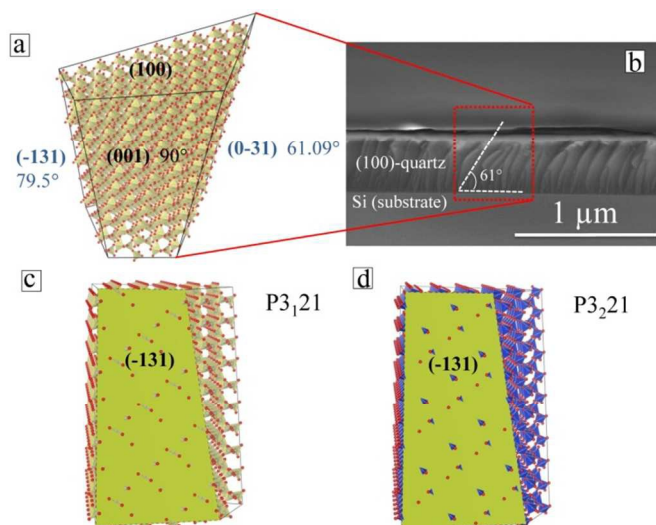

Fig. 3 Crystal morphology of quartz crystallites superimposed on its structural model (a). Cross-section SEMFEG image showing the inclination of the lateral faces in quartz films (b). Representation of the (-131) surfaces in $P3_121$ or $P3_221$ space groups (c, d).

Note that the top faces of h1 and h2 present a definite handedness and closely resemble the specular images of one another. It is therefore natural considering if these distinct habits correspond to quartz crystals of different chirality (i.e. crystallizing in the $P3_121$ and $P3_221$ space groups). However, a direct determination of the chirality of the quartz films is not trivial. In the present case the standard identification of enantiomorphs based in the sense of the rotation imparted to plane-polarized light fails because the small thickness of the films results in rotations (~10^{-4} º) which cannot be reliably detected with conventional systems.

Different enantiomorphs can also be distinguished with dedicated techniques not readily available to us such as anomalous scattering[11] or three-beam X-ray diffraction[12] both requiring synchrotron radiation and crystals of the appropriate size, or circularly polarized Raman spectroscopy which also needs a special setup[13].

Nevertheless, we have exploited the relationships between crystal morphology and crystal structure to get more insight into the chirality of epitaxial quartz films on silicon. It is well known that the crystalline habit is composed by slow-growing faces characterized by a low number of dangling bonds per unit area and a correspondingly low surface energy. We shall see that the surface energies of h1 and h2 habits are substantially different depending on whether we consider crystallization in $P3_121$ or $P3_221$ space groups and we believe that this is a powerful argument supporting the homochirality of the epitaxial quartz films.

We have made a comparative estimation of the surface energies of h1 and h2 in the $P3_121$ and $P3_221$ space groups by evaluating the number of dangling bonds per unit area for each of the surfaces of these habits using the VESTA[14] software (see Fig. 3a and 4).
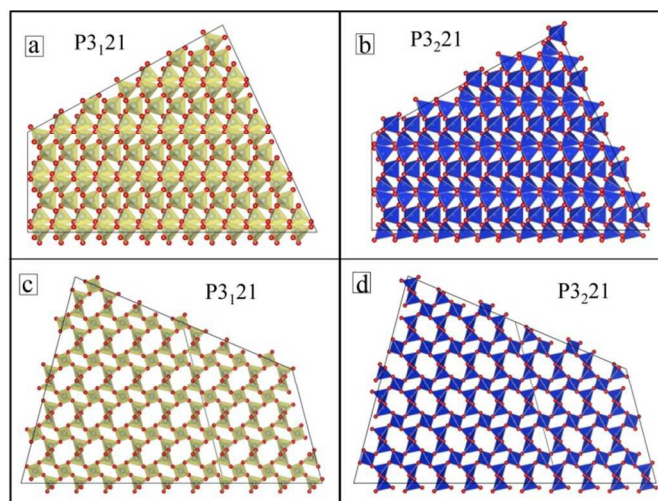

Fig. 4 (100) habit reconstruction from AFM images superimposed on its structural model in $P3_121$ or $P3_221$ space groups (crystal structures are represented by co-ordination polyhedra and gray and red balls represent Si and O atoms, respectively).

Taking into account the strongly covalent character of the silicon-oxygen bonds we have considered complete SiO_4 tetrahedra and we have equated the number of dangling bonds to that of oxygen atoms contained within or above the crystal facets. Let us take the case of h1 to illustrate our point. Fig. 3c and 3d clearly show that the number of oxygen atoms in a (-131) surface with the same area is significantly larger for the $P3_121$ space group than for $P3_221$. In particular we found about 0.06 at./Å^2 for $P3_121$ compared to about 0.04 at./Å^2 for $P3_221$, implying that a h1 habit with a $P3_121$ structure would present (-131) faces with 50% higher surface energy. Similarly, the surface energies of (0-31) and (013) are about 20% and 7% lower for a $P3_221$ structure, while no differences are found in the case of (100), (-100) and (001) surfaces (see images of these surfaces in figure S6 and S7).

The crystallization mechanism underpinning the habit and enantiomorphic selection illustrated in the present work is still under study and far from being understood. However we would like to comment on some aspects that we believe can be relevant to explain this mechanism. In our previous studies on this system we found evidence of a process of competitive growth occurring during the crystallization of the quartz films. Also, the crystallization of amorphous SiO_2 is assisted by alkaline earth ions in a process occurring at high temperatures. In this scenario, we conjecture that the conditions exist for a process of secondary nucleation to operate amplifying enantiomorphic fluctuations, analogously to the mechanism proposed to explain the emergence the enantiomorphic purity in the $NaClO_3$ model system[7, 15].

Conclusions

In this work we have presented a combined AFM study with computer-assisted crystallographic calculations showing the existence of two single trapezoidal habits of epitaxial quartz films on silicon. The estimated number of dangling bonds per unit area for each of the surfaces of these habits provides insight into the homochirality of epitaxial quartz films. Importantly, the number of oxygen atoms in the (-131) surface was significantly larger for the $P3_121$ space group than for $P3_221$. Therefore, our study evidences that these quartz surfaces are likely to be intrinsically chiral and thus, reveals an enantiomer-selective habit of epitaxial quartz films. We believe that this work might open new perspectives in the field of enantioselective surface chemistry and in the mechanisms governing crystallization of chirally pure systems.

Notes and references

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