Aragonite growth on single-crystal substrates displaying a threefold axis†

Boaz Pokroy* and Emil Zolotoyabko

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Aragonite was grown epitaxially under calcite-stable conditions by using carbonate free single-crystal substrates with a threefold axis oriented normal to the surface.

Although biogenic crystals are grown under standard pressure and temperature, they often exist as metastable polymorphs.[1,2] A well-known example is the formation of aragonite (a metastable orthorhombic polymorph of $CaCO_3$) in the nacre layer of mollusc shells.

Various studies (see the brief review[3]) have attempted to answer the fundamental question of why aragonite, which at room temperature is thermodynamically less favorable than calcite (the rhombohedral polymorph of $CaCO_3$) grows during biomineralization. For example, Falini *et al.*[4] and Belcher *et al.*[5] showed that macromolecules extracted from the aragonitic shells can induce *in situ* formation of aragonite. In their pioneering study, Weiner and Traub[6] showed that within the nacre layer the *a* and *b* axes of the β-chitin matrix are aligned with the crystallographic *a* and *b* directions of the aragonite lattice and therefore the nacre layer grows as *c*-oriented. By comparing the distances between Ca ions in the *a*–*b* aragonite plane with some characteristic spacings of the organic matrix, one can find relatively good matching along the *a*-axis, while matching along the *b*-axis of the aragonite structure is much poorer (the misfits are 4.5% and 15.5%, respectively). This finding has raised the basic question concerning the role of proper substrate in the growth of biogenic aragonite.

Addadi *et al.*[7] claimed that the stereochemical effect is another important factor controlling biomineral nucleation. In seashells that effect is revealed in the orientation relations between the carbonate groups of $CaCO_3$ and the carboxylate groups of aspartic acid. For example, Aizenberg *et al.*[8] showed orientation relations between the intracrystalline protein chains and the direction of calcite crystal growth in the *Kebira* spicule. It has also been proven that the orientation of calcite can be controlled stereochemically when it nucleates on self-assembled monolayers.[9] Litvin *et al.*[10] grew aragonite on the C_{16}ISA monolayers, but it is not yet clear whether that growth is the result of a "geometric registry" or of the stereochemical effect.

There is also evidence that in organisms, calcite and aragonite are produced *via* a transient calcium carbonate amorphous phase (see *e.g.* Refs.[11,12]), which provides an optional way for polymorph selection. However, to date there is only one example of aragonite formation *via* this route and only in larval shells.[13]

Recently, Kim *et al.*[14] have grown $CaCO_3$ on three different carbonates of the aragonite group, *viz.* $SrCO_3$, $PbCO_3$, and $BaCO_3$, which have larger lattice parameters than that of $CaCO_3$. Their study was aimed specifically at understanding the effect of lattice mismatch on aragonite formation. They concluded that the lattice mismatch which still permits aragonite growth might be as large as 5.4%, but definitely less than 7.1%. The results demonstrated the substrate's influence on polymorphism in $CaCO_3$, although in Kim *et al.*'s experiment the contributions of lattice mismatch and stereochemical effects cannot be separated because of the presence of the same carbonate groups in the substrate and in the grown layer.

For a deeper understanding of aragonite nucleation we tried to determine the net mismatch effect on aragonite growth, eliminating as far as possible the stereochemical contribution. For this purpose, we used several commercially available high-quality single-crystal wafers free of carbonate groups, namely rhombohedral sapphire (Al_2O_3) and lithium niobate ($LiNbO_3$), trigonal quartz (SiO_2), and cubic silicon (Si). All wafers were cut perpendicular to the threefold axis in order to obtain a trigonal symmetry of cations in the surface plane, which is similar to the local symmetry of Ca ions in the (001) plane (in the hexagonal setting) of calcite and aragonite (see below). The growth of $CaCO_3$ crystals was accomplished on the polished (to optical quality) wafer surfaces. Control experiments were performed using commercially available (001)-oriented Si wafers, (001)-oriented calcite plates, (001)-oriented aragonite crystals (of geological origin), and amorphous silica (SiO_2).

In order to describe the lattice mismatch in non-cubic crystals, more than one parameter is generally needed (see Ref.[15]). However, epitaxial growth of the (001)-oriented rhombohedral (in the hexagonal setting) or hexagonal layer on the (001) plane of a rhombohedral or hexagonal substrate is controlled by a single mismatch parameter, M_1, since the distances between all neighboring cations are equal. In other words, the in-plane Bravais unit cell is a rhomb with equal edges, a_S, and an angle between adjacent edges, $\alpha = 120^\circ$ (see Fig. 1a). In sapphire, lithium niobate, and quartz, $a_S = a$, while in silicon $a_S = a/\sqrt{2}$ (see Table 1). Correspondingly, $M_1 = (a_L - a_S)/a_S$, where a_L and a_S are the rhomb's edges in the grown layer and in the substrate, respectively. In our study, this approach can be applied directly to the calcite growth, since the symmetry of calcite is also rhombohedral, with a = 4.991 Å.[16] The calculated mismatch values, M_1, for epitaxial growth of the (001)-oriented calcite on the substrates in use, are summarized in Table 1.

The case of the epitaxial growth of aragonite is more complicated, since aragonite has an orthorhombic structure, and

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† Electronic supplementary information (ESI) available: XRD and micro-Raman analysis and additional HRSEM images. See http://www.rsc.org/suppdata/cc/b5/b500584a/

*bpokroy@tx.technion.ac.il

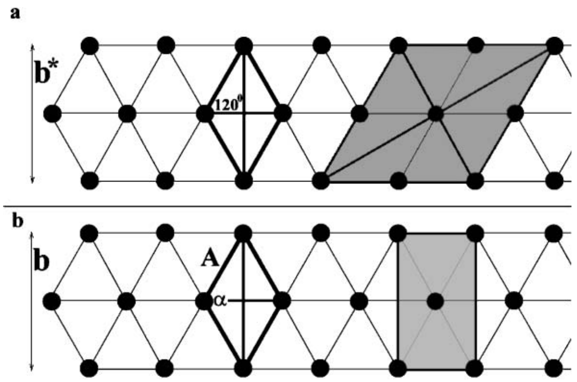

Fig. 1 Cation arrangement in the (001) plane of: (a) – Calcite; the rotated doubled cell, which is used to explain epitaxial growth of aragonite on a (111)-oriented Si wafer, is shaded. (b) – Aragonite; the orthorhombic unit (*a*–*b*) cell is shaded.

two parameters are needed in order to describe lattice mismatch in its (001) plane with respect to two different translations, $a = 4.9620$ Å and $b = 7.9696$ Å.[17] In the (001) plane of aragonite, cations of each type occupy two atomic positions connected by a vector $\frac{1}{2}(a + b)$. The in-plane orthorhombic lattice can be constructed by multiplication of the so-called pseudo-hexagonal Bravais unit cell (see Fig. 1b), which is a rhomb with edges $A = (1/2)\cdot(a^2 + b^2)^{1/2} = 4.694$ Å, and an angle $\alpha = 180° - 2\arcsin[a/(a^2 + b^2)^{1/2}] = 116.2° \neq 120°$. The rhomb diagonals are perpendicular to each other and equal to a and to b. Correspondingly, the two mismatches, $M_a = (a - a_S)/a_S$, and $M_b = (b - b^*_S)/b^*_S$ should be used, which reflect the relative differences between the two rhomb diagonals in the aragonite layer and in the substrate. Note that for the substrate unit cell, the diagonals are a_S and $b^*_S = a_S\surd 3$. The calculated lattice parameters and mismatches for aragonite growth are summarized in Table 1.

$CaCO_3$ crystallization at room temperature (22° ± 2 °C) and normal pressure was accomplished by slow diffusion of CO_2 into 1 ml of 10 mM $CaCl_2$ placed on various substrates. Examined substrates, including the control ones, were cut into pieces nearly 1 cm^2 in area, and placed into the wells of a nunc box and sealed by transparent polyethylene film. After that, exactly the same diffusion outlets were produced in all wells by a 21G needle. This procedure ensured identical crystallization parameters for all samples involved and allowed us to obtain very reproducible results of the crystallization experiments.

Table 1 Lattice parameters of the substrates used as well as the mismatches for the epitaxial growth of the (001)-oriented layers of calcite and aragonite

			Mismatch (%)		
			For calcite growth	For aragonite growth	
Substrate	Lattice parameter a^*_S (Å)	Lattice parameter b^*_S (Å)	M_1	M_a	M_b
Si(111)	3.8404	6.6518	30.0	29.2	19.8
Al_2O_3	4.7587	8.2423	4.9	4.3	−3.3
SiO_2	4.9136	8.5106	1.6	1.0	−6.4
$LiNbO_3$	5.1494	8.919	−3.1	−3.6	−10.6
Calcite	4.991	8.6447	0	−0.6	−7.8

The grown crystals were characterized by X-ray diffraction (XRD), high-resolution scanning electron microscopy (HRSEM), and micro-Raman spectroscopy.

The results of the substrate-assisted crystallization can be summarized as follows. On all substrates displaying a threefold axis, epitaxial aragonite having a (001) preferred orientation (at least in the initial stage of crystallization) was observed, in addition to epitaxial calcite, which was formed predominantly in all cases except the (111)-oriented Si. Selected examples of pseudo-hexagonal (001)-oriented aragonite crystals and (001)-oriented calcite crystals grown on different substrates are shown in HRSEM images (see Fig. 2). The presence of aragonite crystals was confirmed by XRD analysis (see Fig. 4a ESI†). Micro-Raman spectra (see Fig. 4b ESI†) of the pseudo-hexagonal crystals visible in HRSEM also certified that these are of the aragonite polymorph.

Considering the epitaxial growth of aragonite on sapphire, quartz, and lithium niobate, it can be concluded that the crystallization proceeds under mismatches of both signs, the highest being that for lithium niobate, *viz.* $M_b = -10.6\%$ (see Table 1). In all cases the mismatch, M_a, is less than 5%. It should be emphasized that aragonite grows together with calcite, which is not only favorable thermodynamically, but in some cases has less lattice mismatch to the substrate than aragonite (*e.g.* for lithium niobate and quartz). Nonetheless, the proximity of the substrate and the layer lattices plays an important role in the epitaxial growth of aragonite, a fact that was proven by a control experiment using amorphous silica (SiO_2) as a substrate, which showed no traces of aragonite formation.

Aragonite formation on (111)-oriented silicon is intriguing, since the mismatch of 20–30% (see Table 1) is certainly too high for epitaxial growth. Control experiments with (001)-oriented Si wafers did not indicate any aragonite formation, so the atomic arrangement on the (111) plane of Si is a factor of importance to the growth process. We thus had to look for another, larger structural unit of the silicon lattice that would better match the cation array in the (001) aragonite plane. In fact, viewing Fig. 1a, one can find the outline of the rotated double rhomb within the

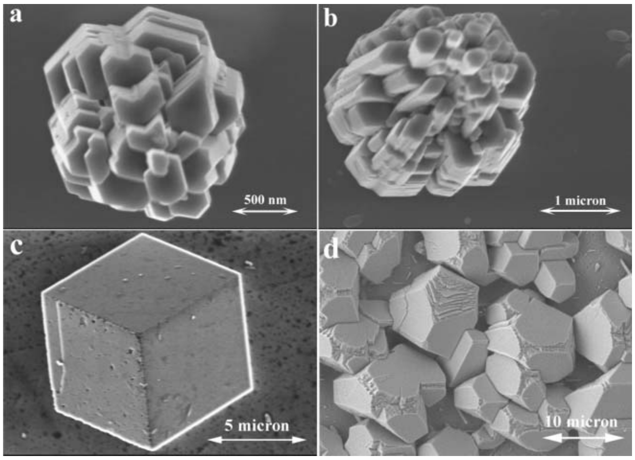

Fig. 2 Selected HRSEM images of $CaCO_3$ crystals as precipitated on different substrates: (a) – (001)-oriented pseudo-hexagonal aragonite on $LiNbO_3$; (b) – (001)-oriented pseudo-hexagonal aragonite on (111)-Si; (c) – (001)-oriented calcite crystal grown on $LiNbO_3$; (d) – (001)-oriented calcite crystals grown on calcite (no aragonite detected).

silicon lattice having diagonals equal to $2a_S$ and $2b^*_S$. The first diagonal nearly fits the lattice parameter, b, of aragonite (misfit, $M_{2a_s} = (b - 2a_S)/2a_S = 3.8\%$), while the second diagonal can be compared to the triple lattice parameter, $3a$, of aragonite (misfit, $M_{2b^*_s} = (3a - 2b^*_S)/2b^*_S = 11.9\%$). Projecting these doubled cells onto the (001) plane of aragonite, we find that the cations of aragonite are located near the silicon atoms or at the centers of right-angled triangles formed by silicon atoms (see Fig. 3). It seems that this arrangement is suitable for aragonite formation. In fact, the misfit of the doubled (111)-Si cell with respect to the calcite lattice is higher ($M_{2a_s} = M_{2b^*_s} = 12.6\%$) than for aragonite, especially when the parameters, M_{2a_s}, are compared. As a consequence, calcite does not grow epitaxially on the (111)-oriented silicon, but aragonite does (see Fig. 5 ESI†).

Further experiments showed that there are situations in which a stereochemical effect controls $CaCO_3$ growth, even if the relevant lattice mismatch is rather small. For example, when growing $CaCO_3$ on (001)-oriented calcite plates, only calcite was observed and no trace of aragonite (see Fig. 2d), although the lattice mismatch for the aragonite/calcite couple is lower than that for the aragonite/lithium niobate couple (see Table 1). At the same time, when growing $CaCO_3$ on (001)-oriented geological aragonite, only aragonite grew epitaxially (see Fig. 6 ESI†), but not calcite, despite calcite's being thermodynamically stable. In this context, we stress again that in experiments for investigating the role of lattice mismatch in $CaCO_3$ polymorph formation, care should be taken to distinguish between the mismatch and the stereochemical effects.

In order better to understand the aragonite growth, we stress that the difference between the heats of the calcite or aragonite formation is only about 1 kJ mol^{-1}.[18] Therefore, a slight change in the system's free energy will facilitate the nucleation of aragonite crystals. This can be achieved by lowering the interfacial energy at room temperature.

A suitable substrate is capable of lowering the interface energy, thus providing conditions for heterogeneous nucleation, which is energetically more favorable than homogeneous nucleation in solution. This lowering is different for each of the polymorphs, aragonite and calcite. Besides that, lattice mismatch between components induces some strain energy, which should be added to the free energy of a nucleating crystal. A combination of these factors plus the difference in the supersaturaion conditions at the nucleation point controls the substrate-assisted nucleation of $CaCO_3$.

It seems that at low mismatches the role of the substrate is, generally, to reduce the barrier between the free energies for aragonite and calcite formation and to render comparable probabilities for nucleation of both types of nuclei. In fact, under the experimental conditions used we did not completely suppress the formation of calcite, but facilitated the concurrent nucleation of aragonite crystals.

When comparing the lattice mismatches in aragonite growth on the different oxide substrates included in Table 1, one can conclude that aragonite grows epitaxially at up to approximately 11% mismatch. That value is significantly higher than the 7.1% mentioned in Ref. [11]. With regard to the investigated substrates, it appears that, up to 11% mismatch, the reduction of interfacial energy, allowing aragonite formation, prevails over the increase in the mismatch-induced strain energy. Certainly, this balance is valid only below some critical thickness, and this explains why our epitaxially grown aragonite crystals were always rather small ($\approx$ 200 nm, which is comparable to the thickness of the individual lamellae in the nacre structure[19]).

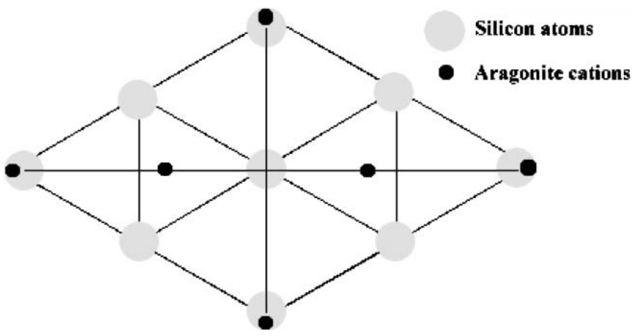

Fig. 3 Proposed orientation relationships between *a–b* oriented aragonite and (111)-oriented Si. Large light circles are Si atoms and small dark circles are Ca^{++} cations.

Experimental results clearly show that aragonite can nucleate and grow *c*-oriented (*i.e.* with the *a–b* plane being the surface plane) on substrates which do not contain carbonate groups, *i.e.* with no stereochemical effect. At the same time, we found that the proximity of cation arrangements in the substrate and the grown layer is an essential factor for the epitaxial growth of $CaCO_3$. This finding could have important implications towards understanding the biomineralization process by which aragonite is formed in mollusc nacre.

Boaz Pokroy* and Emil Zolotoyabko
Faculty of Materials Engineering, Technion – Israel Institute of Technology, Haifa, 3200, Israel. E-mail: bpokroy@tx.technion.ac.il; Fax: 972-4-8295677; Tel: 972-4-8295793

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