PHYSICAL REVIEW B **93**, 020101(R) (2016)

Structure of periodic crystals and quasicrystals in ultrathin films of Ba-Ti-O

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(Received 16 October 2015; published 7 January 2016)

We model the remarkable thin-film Ba-Ti-O structures formed by heat treatment of an initial perovskite $BaTiO_3$ thin film on a Pt(111) surface. All structures contain a rumpled Ti-O network with all Ti threefold coordinated with O and with Ba occupying the larger. mainly Ti_7O_7, pores. The quasicrystal structure is a simple decoration of three types of tiles: square, triangle, and 30° rhombus, with edge lengths 6.85 Å, joined edge-to-edge in a quasicrystalline pattern; observed periodic crystals in ultrathin film Ba-Ti-O are built from these and other tiles. Simulated STM images reproduce the patterns seen experimentally and identify the bright protrusions as Ba atoms. The models are consistent with all experimental observations.

DOI: 10.1103/PhysRevB.93.020101

Quasicrystals have fascinated the materials world since their discovery [1] due to their noncrystallographic symmetries and quasiperiodic translational order. The first quasicrystal reported was in an Al-Mn alloy. While numerous families of quasicrystals have since been found [2], until recently all known physically realized quasicrystals were either intermetallic alloys or soft matter systems [3,4]. This changed in 2013 with the report of a quasicrystal *oxide* by Förster *et al.* [5] in a thin film Ba-Ti-O structure created by a multistep heat treatment of perovskite $BaTiO_3$ deposited on a Pt(111) surface, among other, periodic, structures. The quasicrystalline structure is identified as a dodecagonal quasicrystal by its twelvefold electron diffraction pattern and by scanning tunneling microscopy (STM) images that show bright protrusions separated by a distance of about 6.85 Å, in positions characteristic of a dodecagonal rectangle-triangle-30° rhombus tiling [6]. Additional experimental details distinguish the phase from perovskite $BaTiO_3$. The Ti ions appear to have charge 3+ via photoemission spectroscopy. The overall stoichiometry (including both the quasicrystalline layer and $BaTiO_3$ islands that remain after the heat treatment used to create the quasicrystal) is $Ba_{0.9}TiO_{2.8}$. While these observations give intriguing information about the nature of the quasicrystalline structure, a complete structure determination is lacking. In this Rapid Communication, we give tiling decoration models for the atomic structure of thin film quasicrystalline Ba-Ti-O and its related periodic crystalline structures, fully consistent with experimental observations.

Our tile decoration model for the quasicrystal is shown in Fig. 1(a). The Ba, Ti, and O atoms overlay the topmost Pt layer and project into a plane as shown. Ba atoms occupy the vertices of the tiles. All Ti atoms are threefold coordinated with oxygen. Most oxygen atoms are twofold coordinated with Ti except for those inside the 30° rhombi (henceforth "rhombs"). The tiles join edge-to-edge. The atomic positions of the ideal tile structures match perfectly for triangles to join rhombs and squares; the other tile combinations require a merger of the tile O positions near the shared edge.

Squares, triangles, and rhombs can be combined to produce numerous periodic and aperiodic tilings. The square-triangle-rhomb tiling pattern formed by connecting the bright spots in the STM images [5] bears a striking resemblance to the "C_a" tiling pattern found by Gähler [6], using projection from a higher dimensional space with a concave acceptance region. This tiling (and its sufficiently large periodic approximants) contains only square-triangle, triangle-triangle, and triangle-thin rhomb edges. The Gähler tiling has squares, triangles, and rhombs in the relative frequency $\sqrt{3}+1 : 2\sqrt{3}+4 : 1$. Assuming that this tiling is the appropriate tiling for quasicrystalline Ba-Ti-O, our tile decoration model gives a Ba:Ti:O ratio of $(\sqrt{3}-1)/2 : 1 : (3\sqrt{3}+1)/4$ or a stoichiometry of approximately $Ba_{0.37}TiO_{1.55}$. From x-ray photoelectron spectroscopy measurements [5], it was deduced that there were both Ti^{4+} and Ti^{3+} ions in their sample in the ratio 5:1. Assuming that all the Ti ion in the quasicrystalline film have charge 3+, all the Ti in the $BaTiO_3$ islands charge 4+, and that the quasicrystalline film has the composition found in our model, the overall composition rounds to $Ba_{0.9}TiO_{2.8}$, exactly as determined experimentally [5].

To test the stability of our model, refine the atomic positions, and determine their optimal heights about the Pt(111) surface, we turn to density functional theory (DFT) calculations. DFT calculations were performed using the code [7] VASP [8]. The PBEsol GGA exchange-correlation functional [9] was used, and the plane-wave cutoff was 500 eV. Calculations were performed using one k point, at the origin. A previous hybrid density functional theory study of Ti_2O_3 in the corundum structure shows a spin-paired electronic ground state [10]. To reproduce these results as closely as possible at lower computational cost, we ran spin-unpolarized GGA+U calculations, after tuning the U parameters for Ti and O to reproduce the volume and band gap of corundum

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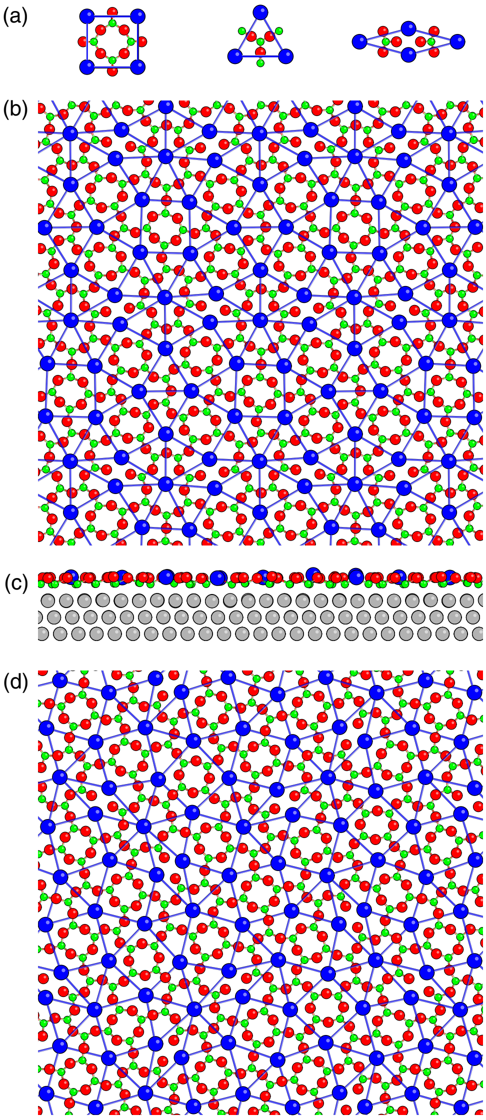

FIG. 1. (a) Decoration of square, triangle, and 30° rhombus (rhomb) tiles. Ba atoms are large blue, Ti small green, and oxygen medium red. (b)–(d) DFT-relaxed structures of Ba-Ti-O quasicrystalline approximants on a Pt-111 surface. Pt atoms are gray. (a) 25.6 Å approximant, top view. (b) 25.6 Å approximant, front view. (c) 49.4 Å approximant, top view.

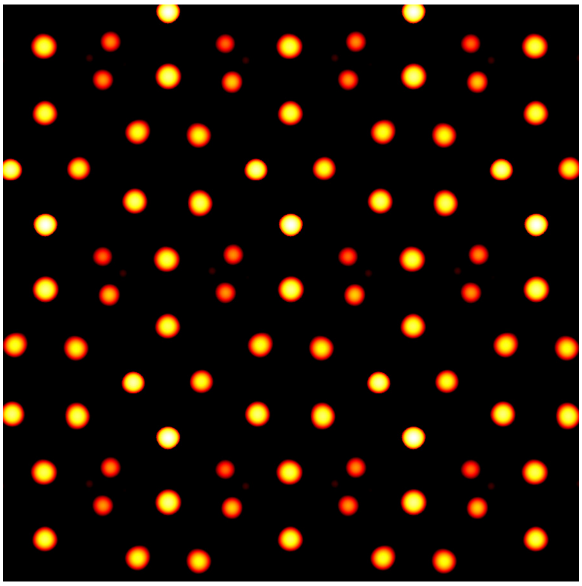

FIG. 2. Simulated scanning tunneling microscopy (STM) topograph of the quasicrystal approximant shown in Fig. 1(b). Simulated bias voltage −0.15 eV, charge density 0.1 e nm^{-3}, and topographic range 1 Å.

Ti_2O_3 as accurately as possible (Ti $U = 2.35$ eV; O $U = 0.30$ eV).

Quasicrystalline structures are not compatible with periodic boundary conditions. To investigate the stability of our model, we turn instead to periodic approximants to the quasicrystalline structure. These periodic approximants have the same local structures as the quasicrystals. One such approximate has a unit cell 25.6 Å on an edge with $\gamma = 120^\circ$. We created an approximate to the Gähler C_a tiling and decorated it as shown in Fig. 1(b). We placed this structure above a model Pt-111 trilayer, strained to have the same periodicity as the approximant. The lowest Pt layer had all atomic coordinates fixed, the next layer z was allowed to vary, and in the topmost layer all atoms coordinates were allowed to move. A vacuum layer was created between the structure and periodic images by using a periodicity of 20 Å in the z direction. The structure was relaxed until all forces were relaxed to less than 0.1 eV/Å. An additional, square, approximant of side length 49.4 Å was created and relaxed on a fixed Pt monolayer until all forces were less than 0.1 eV/Å.

The relaxed structures are shown in Figs. 1(b)–1(d). The structures retain their ideal tile geometries quite well. The most significant distortion is the clockwise or counterclockwise rotation of 3 O around a Ti that frequently occurs. This rotation is often driven by the formation of more favorable O-Ti-O bond angles for the Ti in the thin rhombs; *ab initio* molecular dynamics reveal frequent libration of TiO_3 units at room temperature. The average heights above the topmost Pt layer in the relaxed structure are 3.1 Å, 2.2 Å, and 3.1 Å for Ba, Ti, and O, respectively. Ti-O distances range from 1.80 Å to 1.95 Å. The rumpling of the Ti-O network [Fig. 1(c)] is driven by transfer of electrons from Ba to Pt; the negative surface charge on the Pt layer then attracts the positive Ti ions and repels the negative O ions [11].

STM topographs were simulated using the Tersoff-Hanann approximation [12]. In this approximation, measuring a contour of constant current is equivalent to measuring a contour of constant electron density, projected in the energy range between E_F and $E_F + eV$, with E_F the Fermi level and V the bias voltage. The projected electron density was calculated via DFT, starting with the DFT-relaxed structure in Fig. 1(b). The result is shown in Fig. 2. By comparison with the atomic structure, we see that only the Ba atoms are visible and that the Ti-O network is invisible. The simulated STM image strongly resembles the experimental ones [13]. The sizes of the simulated bright protrusions match even better with experiment if the computed projected charge density is convoluted by an in-plane factor $\exp(-\rho^2/(2\sigma^2)), \sigma = 1.0$ Å, to mimic experimental resolution.

The presence of threefold coordinated Ti atoms in the quasicrystal Ba-Ti-O structure model along with Ti_nO_n polygons

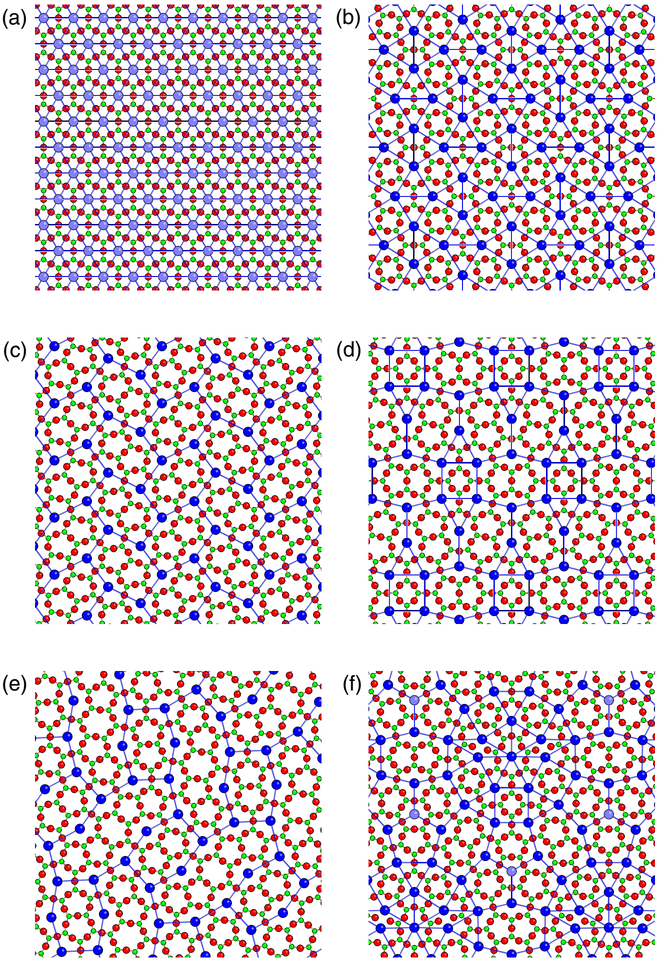

FIG. 3. Structure models for periodic crystalline thin film Ba-Ti-O. (a) Structure model proposed by Wu *et al.* [11] for thin film Ba-Ti-O on Au-111. Light blue color indicates partial Ba occupancy. (b)–(e): Structure models proposed in the present work for various periodic crystalline Ba-Ti-O structures observed by Förster *et al.* [13]: (b) Y-rows; (c) Six-network; (d) Double-Y; (e) Six-tiling; (f) Wagon wheel. There is a partially occupied Ba site shown in light blue.

with $n = 4, 5,$ and 7 is reminiscent of the threefold coordinated network structure observed in other two-dimensional systems such as graphene [14] and bilayer SiO_2 [15,16]. The Ti-O-Ti links in the Ba-Ti-O system are analogous to the C-C bonds in graphene. The Ba-Ti-O counterpart to the ideal graphene structure is shown in Fig. 3(a). This structure has actually been observed by Wu *et al.* [11], from thin film Ba-Ti-O on a Au-111 surface, although the Ba site is not fully occupied.

By assuming that the bright protrusions seen in the STM images of the *periodic* Ba-Ti-O thin film structures observed by Förster *et al.* [13] were Ba, and that the Ti and O formed a Ti-O network with threefold coordinated Ti, we were able to devise a structure model for each case (Fig. 3). A bright spot that is sometimes present and sometimes absent in the STM image of the “wagon wheel” structure [Fig. 3(f)] is easily interpreted as partial Ba occupancy of a Ti_6O_6 pore. The same kinds of tiles that occur in the quasicrystal model, with the same decorations, occur in other structures, but several additional tiles are seen, each with a characteristic decoration: a thin hexagon, a pentagon, and an elongated curved decagon. The “Y-rows” and, arguably, the “Wagon wheel” structures are periodic approximants to the quasicrystal, but the structures in Figs. 3(c)–3(e) are unrelated to the quasicrystal. The Ba:Ti ratios of the periodic crystalline Ba-Ti-O structures in Fig. 3 range from $3 : 13 \approx 0.231$ for the “Six-tiling” to $1 : 3 \approx 0.333$ for the “Y-rows” structure [17] to a hypothetical maximum of 0.5 for Fig. 3(a) with full Ba occupation. The relatively high Ba:Ti ratio of 0.37 for the quasicrystal model described earlier is due to the predominance of tiles with high Ba:Ti ratios.

With such a rich variety of observed structures, it becomes possible to elucidate their common features. Some observations: (1) The Ba-Ti-O systems show Ti_nO_n rings with $n = 4$, 5, 6, and 7 but not $n = 8$ or greater; (2) the $n = 7$ rings are very common and the $n = 6$ rings relatively rare; (3) the 7-rings always share a Ti-O-Ti edge with two or more other 7-rings to create a larger-scale network that can be represented as a tiling; (4) the 7-rings are always occupied by a Ba ion, the 6-rings partially occupied, and smaller rings empty.

The local structure associated with the rhomb in the quasicrystal, its approximants, and the wagon wheel structure can be viewed as the fusion of two Ti_7O_7-type pores to make a dumbbell-shaped pore. The two oxygen atoms that are coordinated with only one Ti serve as a buffer against Coulomb repulsion of the relatively close Ba-Ba pair. An analogous three-dimensional dumbbell-shaped pore was recently found in a zeolite structure [18], and the best structural model in that case similarly had oxygen atoms inside the pore that were bound to only one Si each, instead of the normal two. The analogy with zeolites also suggests one possible application of the structures proposed here: If freestanding monolayers with the structures of the Ti-O networks shown here could be created, they could act as ultrathin filters with a uniform pore size for gas separation, etc.

It remains an open question how the quasicrystal structure of Ba-Ti-O is stabilized relative to approximant and nonapproximant arrangements that can also occur. The fact that these structures form at high temperature suggests that entropy (vibrational and perhaps tiling [19]) may play a key role. In any case, the existence of detailed structure models for all these structures is a first step toward solving this problem.

The authors thank Terrell A. Vanderah (NIST) for helpful discussions. M.M. was supported by Slovak Grant Nos. VEGA 2/0189/14 and APVV-0076-11. C.L.H. received support from DOE Grant No. DE-FG02-89ER45405.

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