

Preferential stability of the d-BCT phase in ZnO thin films

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Stoichiometric B4 thin films have formally divergent surface energies, which arise from the intrinsic dipole of the unit cell. Previous density functional theory studies have predicted that below a critical thickness this results in relaxation to the nonpolar planar h-MgO structure. The calculations presented here demonstrate that h-MgO-structured ZnO thin films are themselves unstable with respect to further relaxation to the d-BCT structure, which restores near-tetrahedral local coordination while minimizing the surface dipole. Although the B4 → h-MgO relaxation is disfavored for slabs thicker than 20 layers, d-BCT is predicted to be the favored polymorph for slabs up to 54 layers. Nudged elastic band calculations and vibrational analysis indicate that the h-MgO → d-BCT relaxation is spontaneous at nonzero temperatures.

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I. INTRODUCTION

Many II-VI and III-V semiconductors adopt tetrahedrally coordinated open structures, usually zinc-blende (B3) or wurtzite (B4), which differ only in the stacking sequence of their interpenetrating close-packed lattices. These materials are wide-band-gap compounds with potential applications in optoelectronic devices such as photovoltaic cells, laser diodes, and photocatalysts. ZnO in particular has been the subject of widespread research, both as an archetypal model system, and due to technologically useful optoelectronic properties.¹ Under ambient conditions ZnO adopts the wurtzite crystal structure. Differing thermodynamic conditions, however, can lead to alternative structures being stabilized, and several have been proposed as existing within a rich polymorphism.² Under compression ZnO undergoes a phase transition to the denser rock-salt (B1) structure,³ and a second transition on the application of further pressure to the CsCl (B2) structure has been observed in molecular-dynamics simulations.⁴ In contrast, negative pressures have been predicted by *ab initio* calculations to stabilize a sequence of more open structures based on zeolite motifs.⁵

Such diversity of potential structures for a single compound provides a range of materials with potentially novel properties. For these alternative polymorphs to be used in technological applications, however, requires they are at least metastable under atmospheric conditions. One approach by which alternative crystal structures can be stabilized is nanoscale synthesis. In nanoscale samples the surface energy can make a significant contribution to the relative stability of competing phases,⁶ and control of surface energies can be used to drive phase transitions between phases which may be otherwise unstable in the bulk.⁷⁻⁹ For example, Decremps *et al.*¹⁰ demonstrated that B1-structured ZnO nanocrystals formed under compression, when subsequently annealed at high pressure, remained metastable when returned to ambient pressure. This was attributed to the stabilizing effect of the low-energy {100} surfaces present in the optimum B1 morphologies. ZnO has a diverse range of growth morphologies, demonstrating topologies such as nanoscale wires, belts,¹¹ or combs.¹² The permutations of surface and bulk energies, offered by this morphological variety, raise the pos-

sibility of stabilizing competing crystal structures under ambient pressure by controlling crystal shapes.

ZnO thin films are one example where finite-size effects have been predicted to modify the relative stabilities of competing crystalline structures.^{13,14} The B4 unit cell is intrinsically dipolar, yet bulk B4 systems preferentially display polar {0001} surfaces, despite the formally divergent surface energy. In macroscopic samples there is considerable evidence that this divergent surface energy is quenched by reconstructive faceting of the surface layers.^{15,16} For thin films below a critical thickness, however, an alternative stabilization mechanism has been proposed. Freeman *et al.*¹⁴ reported density-functional theory calculations that demonstrated that for films below a critical thickness, the B4 structure is unstable with respect to relaxation to a hexagonal planar structure; isostructural with hexagonal boron nitride (BN), and denoted herein as h-MgO (Ref. 17) (Fig. 1). On this basis they proposed that growth of ZnO crystals begins via thin films with the h-MgO structure, which then undergo a transition to the bulk-favored B4 structure when a critical thickness is surpassed, thus explaining the preferential growth of B4 crystals with exposed {0001} surfaces, despite their large formal surface energy.¹³

The distortion of these thin films from the normally favored B4 structure to h-MgO is driven by the decrease in energy associated with quenching the surface dipoles. Below a critical thickness this more than offsets the energetic cost associated with the deformation of the coordination tetrahe-

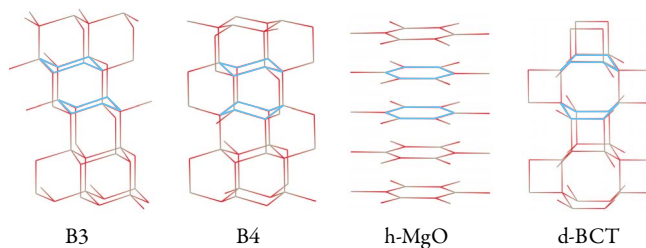


FIG. 1. (Color online) The B3, B4, h-MgO, and d-BCT structures considered as starting geometries for the slab relaxations. Six-membered rings in adjacent *ab* layers are highlighted, showing how the conformation of these and their relative orientation defines each of the four structures.

dra favored in the bulk. For stoichiometric films with thicknesses exceeding the critical limit the increase in bulk energy that would accompany such a relaxation outweighs the decrease in surface energy, and the dipole is predicted to be quenched instead by charge transfer between the $\{0001\}$ surfaces. This screens the intrinsic dipole and gives rise to metallic surfaces.^{13,14}

The relative stabilities of other crystal structures are expected to be similarly dependent on sample thickness, in each case with the balance of bulk and surface energies determining the variation in stability with sample thickness. For dipolar unit cells such as B4, this effect is expected to be acute. This paper reports the results of performing *ab initio* relaxations of periodic thin films with four competing starting structures. The four polymorphs considered are B3, B4, h-MgO, and d-BCT; shown in Fig. 1. All four structures can be described as a network of six-membered rings oriented in the *ab* plane. In the B3 and B4 structures these *ab* six-membered rings have chair conformations, and the relative orientation between alternate layers determines an hcp or ccp stacking sequence. The *ABA* stacking sequence of the B4 structure means the six-membered rings are aligned when viewed along the *c* direction, and a flattening of these rings produces the h-MgO structure, which is isostructural to h-BN, with the ions in trigonal pyramidal coordination environments. This planar structure has previously been predicted to be an intermediate in the B4 \rightarrow B1 pressure-driven phase transition in nanocrystals.^{18,19} Keeping the *ab* six-membered rings aligned, an alternate buckling gives boat conformations, with the boats in adjacent *ab* layers oriented back to back. This gives the alternating four- and eight-membered rings characteristic of the d-BCT structure, which is similar in topology to the BCT (body-centered tetragonal) zeolite structure.

The d-BCT structure has been previously observed in simulations of ZnS nanocrystals to be more stable than the bulk B4 structure,²⁰ and has been predicted as a metastable bulk minimum in LiF.²¹ Molecular-dynamics simulations of ZnO nanorods under uniaxial loading have also produced a pressure-driven B4 \rightarrow d-BCT transition,^{22,23} and the d-BCT structure has been predicted to form spontaneously in down-stroke pressure-driven transitions from B1 nanoparticles containing domain boundaries.²⁴ While the d-BCT structure has not been observed in experimental samples, it is closely related to the IDB* domain boundary,²⁵ which allows the inversion of the *c* direction in a B4 crystal. The IDB* boundary can be considered as a two-dimensional (2D) d-BCT region, with a thickness of a single unit cell. Such boundaries have been implicated in the relaxation of dipoles in simulated B4 nanocrystals,²⁶ and have been observed with high-resolution electron microscopy in a range of materials, including ZnO.^{27,28}

II. CALCULATION METHODS

For each of the four crystal structures slab thicknesses of 4–36 layers were considered. These layers are counted such that each *ab* layer of distorted six-membered rings in the B3, B4, and d-BCT slabs is considered to be two layers, follow-

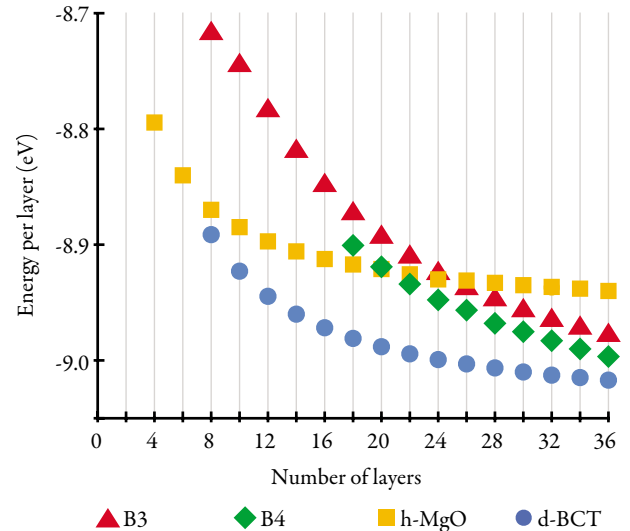


FIG. 2. (Color online) Plot of the calculated energies per layer ($E_{\text{total}}/n_{\text{layers}}$) against slab thickness for relaxed B3, B4, h-MgO, and d-BCT slabs.

ing the convention adopted by Freeman *et al.*¹⁴ The surfaces are separated by a vacuum gap of 15 Å along the *z* direction to give a pseudo-2D periodic system. Results for the B3 slabs are only reported for 8+ layers, since this is the minimum number of layers required to differentiate the *ABA* stacking of B4 from the *ABC* stacking of B3.

Geometry optimizations were performed using density-functional theory as implemented in VASP.^{29,30} This used the gradient corrected exchange-correlation functional of Perdew, Burke, and Ernzerhof.³¹ The energy cutoff for the plane-wave basis set was 500 eV and a $8 \times 10 \times 1$ Monkhorst-Pack *k*-point grid was employed, with the third vector parallel to the slab normal. The interactions between the valence and core electrons, Zn: [Ar], O: [He], were treated using the projector augmented wave (PAW) method.³² Real-space projection was employed for the PAW functions, with projection operators optimized to give an accuracy of $\sim 1 \times 10^{-4}$ eV atom⁻¹, and sufficient *G* vectors were included in the summation for Fourier transforms between real and reciprocal spaces that wrap-around errors were avoided. During geometric optimization the in-plane *a* and *b* lattice parameters were varied to achieve an in-plane pressure of smaller magnitude than 1.0 kbar.

III. RESULTS

The energies of the geometry optimized slabs for each of the four polymorphs are shown in Fig. 2, plotted as the energy per molecular unit against the number of layers; for the unit cells considered here this is equal to number of molecular units. All four polymorphs show the same general behavior with per layer energies that decrease as the total number of layers increases, corresponding to the decreasing contribution from the surface regions and convergence toward the asymptotic bulk energies. The B3 slabs were found to be metastable at all thicknesses considered, but up to 24 layers were the least energetically favorable of the four structures.

At 24 layers the per layer energy of the B3 slabs falls below that of h-MgO. For moderately thick slabs (>14 layers) the general trend of the B4 energies follows that for B3, as expected due to the similarity in structures, but offset to lower energy, due to the favored stability of B4 over B3 for bulk ZnO. For thin slabs (<16 layers) B4 spontaneously relaxes to h-MgO, as reported previously.¹⁴ B4 is able to undergo this relaxation since the h-MgO structure can be formed by a simple flattening of the *ab* chairs that define B4, as is seen in the compression of B4 nanocrystals as an intermediate in the $B4 \rightarrow B1$ phase transition.^{18,19} Equivalent flattening is not energetically favorable for the B3 structure due to the *ABC* stacking sequence, making these B3 slabs metastable at all thicknesses.

For thin films the energy of the nonpolar h-MgO is much lower than that of polar B3 and B4, as expected from the smaller surface energy, which dominates for very thin films. The distortion to trigonal coordination that defines the planar h-MgO structure, however, gives a large bulk energy, and as the slabs increase in thickness they become metastable with respect to both B4 (at 22 layers) and B3 (at 26 layers). B4 slabs with thicknesses of 18 and 20 layers were found to be metastable despite being higher in energy than corresponding h-MgO slabs.

For four and six layer slabs the optimized d-BCT and h-MgO slabs are indistinguishable. The boats of the d-BCT structure relaxed by flattening toward a more planar structure, and the h-MgO planar hexagons relaxed by slightly puckering. For thicknesses where there was a difference in final structures between h-MgO and d-BCT (>6 layers), the d-BCT slabs were lowest in energy. This is due to the unique combination among the considered structures of a nonpolar unit cell; giving low surface energies; and near-tetrahedral coordination; giving a lower bulk energy than h-MgO.³³

The slopes of the four per layer energies at large numbers of layers show that for sufficiently thick slabs the energy of B4 will fall below that of d-BCT to become the favored polymorph, recovering the behavior of the bulk material. The point at which the stability of d-BCT and B4 switches was estimated by fitting total energies for the two data sets for $n_{\text{layers}} > 18$ to a straight line of the form $E_{\text{total}} = E_{\text{surf}} + n_{\text{layers}} E_{\text{bulk}}$. This gross approximation assumes that surface relaxations extend over a negligible thickness, and that the variation in lattice parameters in the surface plane afforded by the zero-strain relaxation are also minimal (hence the surface energy can be treated as constant). This yielded approximate bulk energies per formula unit of $E_{\text{bulk}}(\text{d-BCT}) = -9.053$ eV and $E_{\text{bulk}}(\text{B4}) = -9.092$ eV. This compares well with zero-pressure bulk energies of -9.054 and -9.100 eV per formula unit.³⁴ The approximate surface energies, obtained as the intercepts at zero layers for these fitted lines, are $E_{\text{surf}}(\text{d-BCT}) = 0.035$ eV \AA^{-2} and $E_{\text{surf}}(\text{B4}) = 0.092$ eV \AA^{-2} . These lines cross at $n_{\text{layers}} = 56$ and the d-BCT films are expected to be stable with respect to the B4 structure up to this thickness.

Since for all relaxed slabs with thicknesses greater than six layers the d-BCT structure is both distinct from h-MgO and lower in energy, it is interesting to consider the degree of kinetic stability of the h-MgO structure. Transition pathways between the ten-layer h-MgO and d-BCT structures were cal-

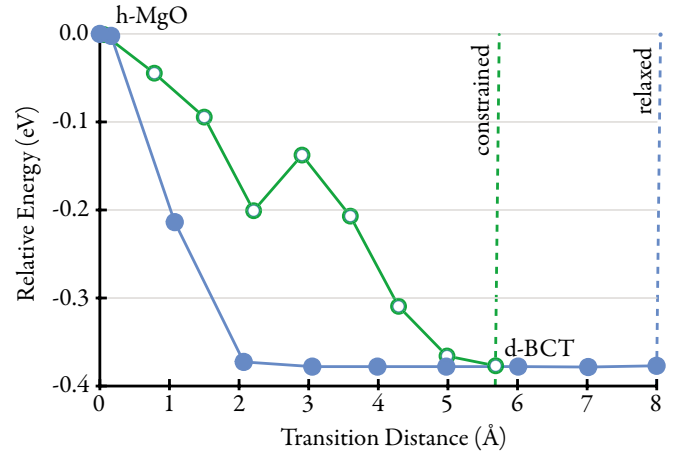


FIG. 3. (Color online) Energy pathways from nudged elastic band calculations for a ten-layer slab from the h-MgO to d-BCT structures. The start and end structures for both pathways are the optimized zero-pressure h-MgO structure, and the optimized zero-pressure d-BCT structure.

culated using nudged elastic band calculations. As shown in Fig. 4, the in-plane lattice parameters vary between the polymorphs, and it is thus necessary to interpolate the change in surface area when considering intermediate points along the transition pathway. Two pathways were considered, which have their energy profiles shown in Fig. 3. The green (constrained) pathway is for *ab* lattice dimensions that are linearly interpolated between those of the start and end points, while the blue (relaxed) pathway is calculated with each intermediate image allowed to relax in the *ab* directions, under the usual constraints of the interimage elastic forces. The transition distance at each point is the sum of distances between all previous pairs of adjacent images, hence the relaxed pathway covers a longer total distance than the constrained pathway. For both pathways the h-MgO structure is the highest point on the energy profile, suggesting little or no barrier exists as the system moves away from the planar h-MgO geometry. Interestingly the constrained pathway shows a local minimum at $\sim 2\text{\AA}$, suggesting intermediate structures can be stabilized under specific in-plane lattice parameters. In contrast, the “relaxed” pathway shows no such intermediate barrier, and the system energy falls to the d-BCT energy after only a short distance along the transition pathway. This suggests that despite being metastable, the h-MgO slabs display very little kinetic stability, and an appropriate distortion toward the d-BCT structure need only be small for the continued relaxation to be spontaneous. Calculation of vibrational modes for the optimized ten-layer h-MgO structure, using finite difference methods and positional offsets of 0.1\AA , predicted one vibrational mode with an imaginary frequency, supporting the interpretation that the h-MgO films are highly unstable.

IV. CONCLUSIONS AND DISCUSSION

Density-functional theory optimizations were performed for B3, B4, h-MgO, and d-BCT slabs with thicknesses in the

range of 4–36 layers. For very thin slabs (<20 layers) the energy ordering is $E(\text{B3}) > E(\text{B4}) > E(\text{h-MgO}) > E(\text{d-BCT})$. As slab thicknesses increase, the energy of first B4 and then B3 falls below that of h-MgO, whereas d-BCT is predicted to be the most stable of these four polymorphs across the studied range. Extrapolation of the slab energies predicts that d-BCT remains optimally stable up to a thickness of 54 layers. This has implications for the growth process of such films, which may proceed via the d-BCT structure, rather than the h-MgO \rightarrow B4 process previously suggested.^{13,35}

This possibility means it is interesting to consider the d-BCT \rightarrow B4 transition. One-potential pathway for this process is d-BCT \rightarrow h-MgO \rightarrow B4, for which the kinetic barrier is determined by the d-BCT \rightarrow h-MgO energy difference.³⁶ For the thick-film limit this is 0.08 eV per molecular unit, and therefore expected to be thermally accessible. This might be expected to be a “worst-case” transition pathway, since it is both highly cooperative, and takes no account of defects. In addition the instability of the h-MgO structure suggests the existence of pathways via lower-energy transition states. This therefore gives an estimated upper limit to the d-BCT \rightarrow h-MgO kinetic barrier.

The predicted stability of the d-BCT structure to moderate thicknesses may also indicate the possibility of growing pure d-BCT samples under appropriate synthetic conditions, although differences in entropy terms between competing polymorphs might influence the stability ordering in experimental samples. This result is expected to apply generally for materials that adopt B4 in the bulk, although the relative stabilities of the different polymorphs will be strongly material dependent, and less polar materials than ZnO may favor d-BCT within much smaller regimes of film thickness.

It is of course possible that other potential structures may exist with lower energies than d-BCT for thin films. For single-crystal samples, it is expected that such favored structures need to be both nonpolar and have near-tetrahedral coordination. One limitation of this study, due to computational expense, is the periodicity enforced by the use of $1 \times 1 \times z$ calculation cells. It is possible that lifting the artificial periodicity may permit arrangements such as those seen in relaxed B4 nanocrystals, where IDB* grain boundaries separate oppositely oriented B4 domains.^{26,37} In addition, the prediction of preferential growth of thin films with the d-BCT structure presented here is based on models of free-standing films. Any films grown epitaxially will be affected by the presence of the support, although the differences in ab lattice parameters among the polymorphs (Fig. 4) suggests that a suitable choice of support might be used to direct the growth of epitaxial films toward selected polymorphs. Such control of crystal growth through epitaxial strain might be the reason for the observation of Tusche *et al.*³⁸ that for ZnO grown on Ag (111) for very thin films the h-MgO structure was formed. The surface lattice parameters for Ag (111) and ZnO

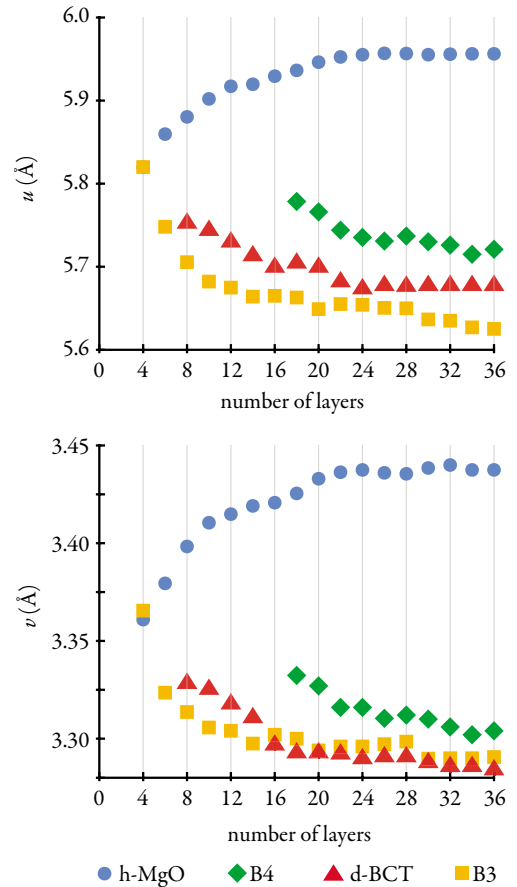


FIG. 4. (Color online) Lattice parameters $\{u, v\}$ for the optimized h-MgO, B4, d-BCT, and B3 slabs.

(0001) differ by 12%, and a coherent (1×1) epitaxial match is disfavored and not observed in experiment.³⁹ The sample described by Tusche *et al.* was indexed to a 7/8 coincidence, which requires an epitaxial strain for ZnO (0001) of 1.6% compared to the bulk lattice parameters. The preferential formation of h-MgO for very thin films is consistent with the larger in-plane lattice parameters required by the flat hexagons that characterize this structure, although other factors might also cause the Ag epitaxial support to affect the relative energies of any potential ZnO structures and ultimately be responsible for the observed growth of h-MgO.

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