Nanofilm versus Bulk Polymorphism in Wurtzite Materials

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We generate a wide range of hexagonal sheet-based ZnO polymorphs inspired by enumeration of their characteristic underlying nets. Evaluating the bulk and nanofilm stabilities of these structures with *ab initio* calculations allows for an unprecedented overview of (nano)polymorphism in wurtzite materials. We find a rich low energy nanofilm polymorphism with a totally distinct stability ordering to that in the bulk. From this general basis we provide new insights into structural transitions observed during epitaxial growth and predictions for nanofilm stability with varying strain or thickness.

Size reduction of inorganic materials to the nanoscale often induces alternative atomic ordering, or polymorphism, relative to the most stable bulk crystal [1]. Nanoscale thin films are attractive well-defined systems to study this effect for theory and experiment. The (nano) technologically [2] important wide band gap wurtzite (wz) semiconductor ZnO, for example, exhibits polymorphism in [0001]-oriented nanofilms on Ag(111) [3] and Pd(111) [4]. For ≤ 3 monolayer (ML) thickness, these supported nanofilms have [0001]-stacked graphitelike flat hexagonal layers with the stacking order of hexagonal BN. This layered form of ZnO (layered-ZnO) was first predicted to be more stable than wz-ZnO in density functional (DF) calculations for free-standing nanofilms ≤ 9 MLs [5]. The structure of layered-ZnO appears to be driven by the elimination of the energetic cost of the electric dipole due to ionic ordering in the stacking direction in nonreconstructed [0001]-oriented wz-ZnO films. Recent theoretical work has highlighted epitaxial strain as a possible means to stabilize supported layered-ZnO nanofilms for >9 MLs [6]. Other DF studies of unsupported nanofilms have showed that the BCT-ZnO [7] structure is more stable than layered-ZnO and nonreconstructed wz-ZnO for [0001]-stacked nanofilms for 4–18 MLs [8]. The lack of (0001) basal plane trigonal symmetry in BCT-ZnO, however, is incompatible with epitaxial growth on (111) surfaces of fcc metals [6] and other substrates would be required [9]. Although BCT-ZnO is not a likely competing phase in experiments where layered-ZnO has thus far been observed, its relevance as a structural modification is highlighted by its observation at reconstructed ZnO (101-0) surfaces [10] and, as a predicted phase in strained wz-ZnO nanorods [11]. Considerably expanding the handful of previously considered nanofilm polymorphs, we report over 20 ZnO polymorphs in both nanofilm and bulk form providing us with an unprecedented overview of the (nano) structural and energetic possibilities of this important material. We show that (i) the stability range of nanofilms and

their energetic ordering are radically different than that of bulk polymorphs, (ii) there exist at least three nanofilm structures with trigonal basal plane symmetry compatible epitaxial growth on fcc metal (111) surfaces that are more stable than layered-ZnO, (iii) BCT-ZnO is one of many structurally related and near energetically degenerate polytypic phases, (iv) with increasing thickness atomically reconstructed wz-ZnO becomes more stable than BCT-ZnO for ~14 MLs, and is always more stable than nonreconstructed wz-ZnO, and (v) BCT-ZnO and layered-ZnO nanofilms are unstable to novel polymorphs under in-plane strain.

For all nanofilm and bulk structures, all unit cell parameters were optimized with all atoms optimized (forces <0.01 eV/Å^{-1}) with periodic DF calculations employing the PW91 functional [12], using the VASP code [13]. The projector augmented wave approach [14,15] was used to describe the effect of core electrons on valence states, with the latter represented by a plane wave basis with a 500 eV cutoff. Nanofilms were separated by over 10 Å in the *c*-stacking direction to avoid spurious periodic interactions. Reciprocal space *k*-point sampling was achieved through appropriate Monkhorst-Pack grids [16]. All nanofilms have between 32 and 128 atoms per cell, with supercell tests (up to 3×3) showing that all energies were converged to <0.0005 eV/ZnO. We generate 24 polymorphic structures [17] using a bottom-up methodology based on nets first used to enumerate and classify bulk silicates having structures based on perpendicular linkages between two-dimensional hexagonal sheets [18]. Following the connectivity of the ten such nets in Ref. [17] with Zn-O bonding, we could generate nine distinct relaxed bulk ZnO polymorphs (including layered-ZnO, wz-ZnO, and BCT-ZnO). Such polymorphs have been predicted to be relatively stable bulk phases for wurzite materials [19] and silicon [20]. For our remaining 15 polymorphs, we created new nets based on mixing together the "primary" nets which generated the nine stablized polymorphs. New mixed nets were biased to those containing primary nets

which previously generated more stable polymorphs. Using this method to search for stable nanofilm polymorphs has specific considerations: (i) a net which generates one bulk polymorph can often generate two [0001]-oriented nanofilms depending on the bulk cut, (ii) energetically detrimental polar surfaces can be avoided by consideration of the connectivity of the generating net.

We first focus on 4 ML ZnO nanofilms, where experiments have not yet discerned a definite preferred atomic structure. Although nonreconstructed wz-ZnO is structurally unstable at this thickness (spontaneously converting into layered-ZnO) all other polymorphs either preserved their structure or converged to structures other than layered-ZnO. Unlike unreconstructed wz-ZnO, all other considered polymorphs have no dipole in the [0001] stacking direction. In a fully ionic picture the dipole in wz-ZnO can be quenched by atomically reconstructing the polar surfaces such that 25% of the charge on both terminating surfaces is compensated [21]. Structural relaxation and/or internal charge transfer may also assist dipole reduction [22] as in DF calculations of nonreconstructed wz-ZnO nanofilms [5,23]. Attempting to stabilize the wz-ZnO structure in 4 ML nanofilms, we transferred 25% of the Zn (O) ions from the (0001)-Zn(O) surface to the (000$\bar{1}$)-O(Zn) surface, both as separated ions, and following experimental reconstruction patterns for bulk surfaces [24,25] In all cases atomically reconstructed wz-ZnO 4 ML nanofilms were found to be >0.08 eV/ZnO less stable than other 4 ML nanofilms considered.

In Fig. 1(a) we compare the energetic stabilites of 4 ML nanofilms and the corresponding bulk phase for a wide range of polymorphic structures, relative to the most stable nanofilm or bulk phase, respectively. For any single polymorph the nanofilm stability is typically lower than in the bulk by ~0.1 eV/ZnO. We highlight two important general features: (i) the energy scale spanned by 4 ML nanofilms (0.04 eV/ZnO) is over four times smaller than that of the corresponding bulk structures (0.17 eV/ZnO), (ii) a significant stability reordering of corresponding structures occurs between 4 ML nanofilms and the bulk. The former suggests that interchanges between different polymorphs should be easier in nanofilms than in the bulk. On the ZnO (0001) surface, competition between nearly energetically degenerate reconstructed structures is found to be strongly dependent on temperature and the oxygen environment [26]. Our stoichiometric 0K structures provide a good starting point to explore such effects in nanofilms. The latter feature implied by Fig. 1(a) is that thin nanofilms are more likely to exhibit non-wz-ZnO phases. The most dramatic bulk-to-nanofilm energetic reordering occurs in the wz-to-BCT stability crossover. Using these two polymorphs as indicators of bulk and nanofilm stability, respectively, we can predict whether the energetic reordering in ZnO is general to other materials. The wz-to-BCT stability crossover can be quantified via the bulk-to-4ML-nanofilm destabilisation energy difference ($\Delta E_{\text{bulk}\rightarrow\text{nano}}$, i.e., $E_{\text{nanofilm}} - E_{\text{bulk}}$, in eV/ZnO), being considerably lower for BCT-ZnO than for wz-ZnO. In Fig. 1(b) we plot the
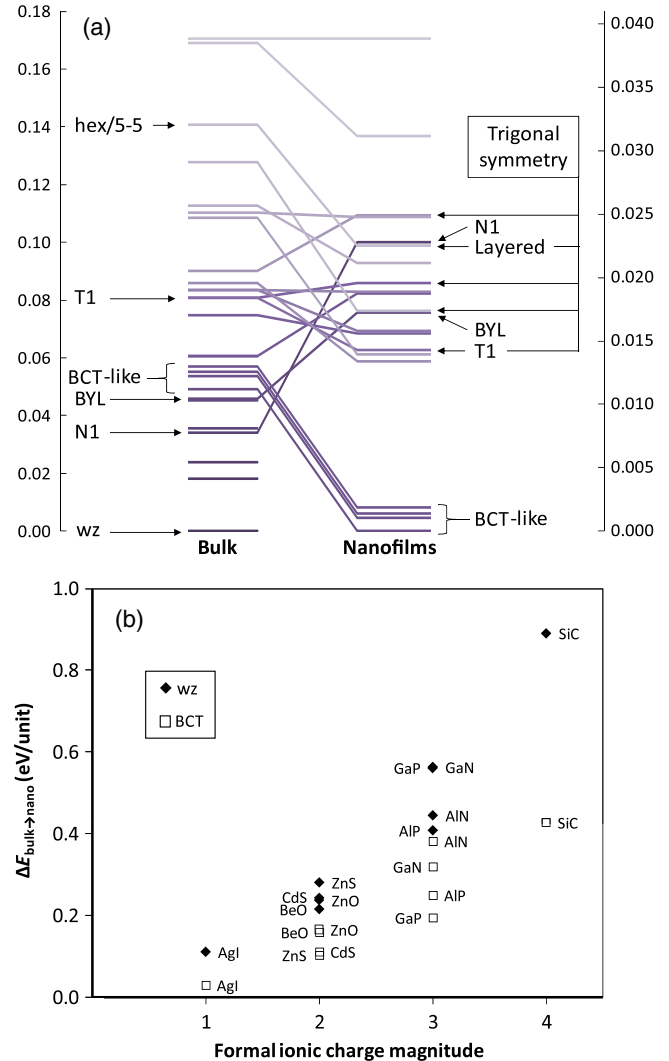

FIG. 1 (color online). (a) Comparison of relative energies (eV/ZnO) of ZnO polymorphs as bulk and 4 ML nanofilms. Right and left energy *y* axes relate to bulk and nanofilm energies, respectively. (b) $\Delta E_{\text{bulk}\rightarrow\text{nano}}$(eV/unit) for wz and BCT for ten wurtzite materials.

$\Delta E_{\text{bulk}\rightarrow\text{nano}}$ for BCT and wz for ten materials showing that BCT is always less destabilized than wz such that a bulk-to-nanofilm stability crossover always occurs. The extent of the crossover is material specific, with $\Delta E_{\text{bulk}\rightarrow\text{nano}}$ linearly increasing relative to a material's formal ionic charge [with $\Delta E_{\text{bulk}\rightarrow\text{nano}}(\text{wz}) > \Delta E_{\text{bulk}\rightarrow\text{nano}}(\text{BCT})$ for all materials]. This strongly indicates that our findings for ZnO are applicable to many other materials. In the remainder we explore various physical implications suggested by the unique overview provided by Fig. 1(a).

Consistent with previous studies the most energetically stable 4 ML nanofilm has the BCT-ZnO structure. Within a very small energy range above BCT-ZnO for both bulk phases (0.01 eV/ZnO) and nanofilms (0.0025 eV/ZnO), we find three other structures. We call these structures BCT-like as they can be regarded as polytypes (i.e., different stacking sequences of structurally similar infinite

two-dimensional layers [27]) with the constituent layers being parallel to the c axis. Polytypism also occurs in the stacking of the $a - b$ aligned hexagonal layers with wurtzite (aligned stacking) and zinc blende (antialigned stacking) being the end members. For BCT-like structures, BCT is one end member with aligned layer stacking, with an antialigned layer stacked structure (which we name BCT-ω, see Fig. 2) forming the other end member. Stacking variations allow potentially infinite possibilities, each giving rise to a distinct BCT-like polytype. Although close in energy, no structural changes in BCT-ω occurred in classical NPT molecular dynamics calculations (1 atm and 300–500 K for 100 ps), using dedicated potentials [28] and the GULP code [29]. The dynamically stability of BCT-like polytypes (and c-stacked polytypes) may be due to the energetically expensive requirement of wholesale changes in bonding between all aligned layers for interconversions.

Although having high stabilities, due to their lack of trigonal (0001) basal plane symmetry, the BCT-like ZnO nanofilms are unlikely to explain the experimental observation that the fcc metal-supported layered-ZnO phase disappears for ≥ 3 ML [3,4]. Unlike the observed of Zn deficiency on bulk-terminated polar (0001)-Zn surfaces [25], in Ref. [3], the 1:1 ZnO stoichiometry was kept fixed within all layers indicating that any dipole reduction is via another mechanism. The good structural agreement between experiment and theoretical calculations for free-standing layered-ZnO nanofilms [5] for the very thin 1–3 ML regime, indicates that metal support has a minor effect on nanofilm structure. Calculations on 1 ML layered-ZnO supported on Ag(111) [30] also show no indication of metal-ZnO charge transfer, confirming the rather passive role of the Ag support. The experimentally prepared
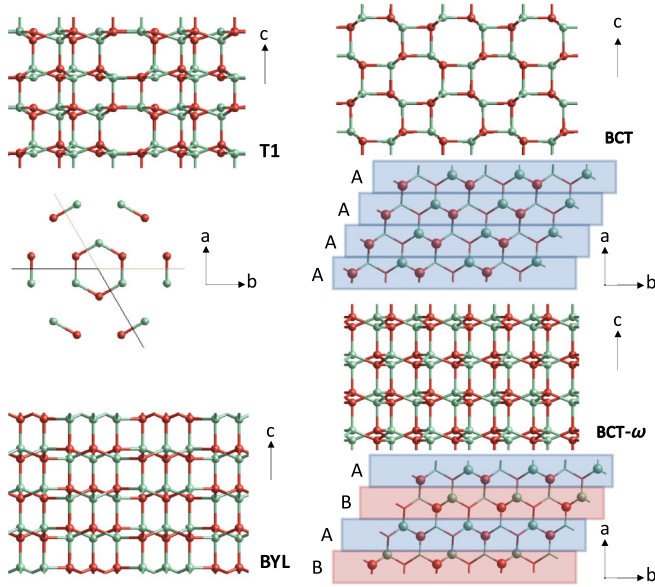
3.5 ML ZnO Ag(111)-supported nanofilm has a 55% 4 ML coverage (the third ML coverage being 5% under complete), and thus is formed by 50% of stoichiometric 4 ML ZnO.

Considering our set of stoichiometric nonpolar 4 ML nanofilms, we find three which have trigonal (0001) basal plane symmetry and are more energetically stable than layered-ZnO. The most stable of these (T1) is labeled in Fig. 1 (see also Fig. 2). In Table I we compare the calculated structures of T1-ZnO and layered-ZnO 4 ML nanofilms and bulk wz-ZnO with the experimental interlayer structural data for the 3.5 and 4.5 ML samples from Ref. [2]. For interatomic distances between layers 1 and 2 in both 3.5 and 4.5 ML experimental samples, the best match with the calculated data is mainly for 4 ML layered-ZnO.

Following Ref. [3] this strongly indicates that this polymorph dominates the first two MLs. For layers 3 and 4 the interatomic Zn-O and Zn-Zn distances strongly point to an alternative structure in both samples, with the calculated bulk wz-ZnO interlayer distances matching well with experiment. Although free-standing 4 ML wz-ZnO nanofilms are inherently structurally unstable, it is perhaps possible in experiment that epitaxial effects and/or charge transfer from the support may help to stabilize more bulklike 4 ML nanofilm structures. Alternatively, the experimental data may point to another polymorphic structure for the 3.5 and/or 4.5 ML nanofilms. In Table I, the calculated interlayer data for the T1-ZnO 4 ML nanofilm shows good agreement with the experimental data for the interatomic distances between layers 2 and 3, particularly for the 4.5 ML sample. Allowing for the estimated experimental error (± 0.1 Å) an interpretation of the experimental data for layers 2 and 3 by layered-ZnO or wz-ZnO may also be possible. However, that there is at least one other candidate nanofilm structure that is fully compatible with the experimental interlayer data opens the possibility that such polymorphs could play a role in the observed structural instability of metal-supported ZnO for >2 ML [3,4].

FIG. 2 (color online). Selected polymorphs. Top left: T1 with its trigonal basal plane, bottom left: BYL, right: BCT (upper) and BCT-ω (lower) with respective c-aligned stacking sequences.

TABLE I. Comparison of differences in calculated structural data [interlayer Zn-Zn ($d_{\mathrm{Zn\text{-}Zn}}$) and Zn-O ($d'_{\mathrm{Zn\text{-}O}}$) distances] for layered-ZnO and T1-ZnO 4 ML nanofilms and bulk wz-ZnO with experimental data for 3.5 and 4.5 ML [3]. Best matches are underlined.

	3.5 ML			4.5 ML		
	Layer 1-2	Layer 2-3	Layer 3-4	Layer 1-2	Layer 2-3	Layer 3-4
$d_{\mathrm{Zn\text{-}Zn}}$(Å)						
Exp.	2.30	2.53	2.66	2.25	2.54	2.62
Layered	0.00	−0.15	−0.36	0.05	−0.16	−0.32
T1	0.18	−0.05	−0.18	0.23	−0.06	−0.14
wz (bulk)	0.35	0.12	−0.01	0.40	0.11	−0.03
$d'_{\mathrm{Zn\text{-}O}}$(Å)						
Exp.	2.27	2.40		2.10	2.26	
Layered	0.06	−0.03		0.23	0.11	
T1	−0.13	−0.18		0.04	−0.03	
wz (bulk)	−0.26	−0.39		−0.09	−0.25	

Relative nanofilm structural stability can also be influenced by thickness. A previous study showed that BCT-ZnO is more energetically stable than layered-ZnO and unreconstructed wz-ZnO from 4–18 ML [8]. From Fig. 1 we can choose a structure having an energetic stability between BCT-ZnO and layered-ZnO for 4 ML, and between wz-ZnO and BCT-ZnO in the bulk phase (e.g., N1 or BYL [31] in Fig. 1). We can then predict that at some nanofilm thickness >4 ML this phase will be more energetically favored than ZnO BCT. In Fig. 3(a) we plot the energetic stability of BYL-ZnO (see also Fig. 2) and that of BCT-ZnO relative to nanofilm thickness. Extrapolating from the calculated data points for 8, 12, 16, and 20 ML, we predict a crossover at a thickness of approximately 26 ML at which BYL-ZnO [blue line, Fig. 3(a)] will be more stable than BCT-ZnO [gray line, Fig. 3(a)]. Following previous work [5,6,8], we also include unreconstructed wz-ZnO films (structurally stable for >9 ML only) for comparison [green line, Fig. 3(a)]. We find that the BCT-to-BYL crossover occurs

slightly before the thickness at which it is estimated that unreconstructed wz-ZnO becomes more stable than BCT-ZnO (~28 ML [8]). We also consider reconstructed wz-ZnO nanofilms. Although for 4 ML we could not stabilize the wz-ZnO structure, for ≥ 8 ML nanofilms atomic reconstruction can stabilize the wz-ZnO structure. Here we employ a simple individual ion transfer approach to quench the dipole in the 8–20 ML wz-ZnO nanofilms. As expected from our attempts with 4 ML nanofilms, 8 ML free-standing atomically reconstructed wz-ZnO nanofilms are considerably less stable than most other nanofilms (e.g., BCT-ZnO or BYL-ZnO). For increasing thickness, however, the stability of such nanofilms rapidly increases such that atomically reconstructed wz-ZnO becomes the most energetically stable ZnO phase for >16 ML [red line, Fig. 3(a)], well before either BYL-ZnO or unreconstructed wz-ZnO nanofilms start to energetically compete with BCT-ZnO. For all thicknesses considered, and by extrapolation, for all thicknesses ≥ 9 ML, our results imply that atomically reconstructed
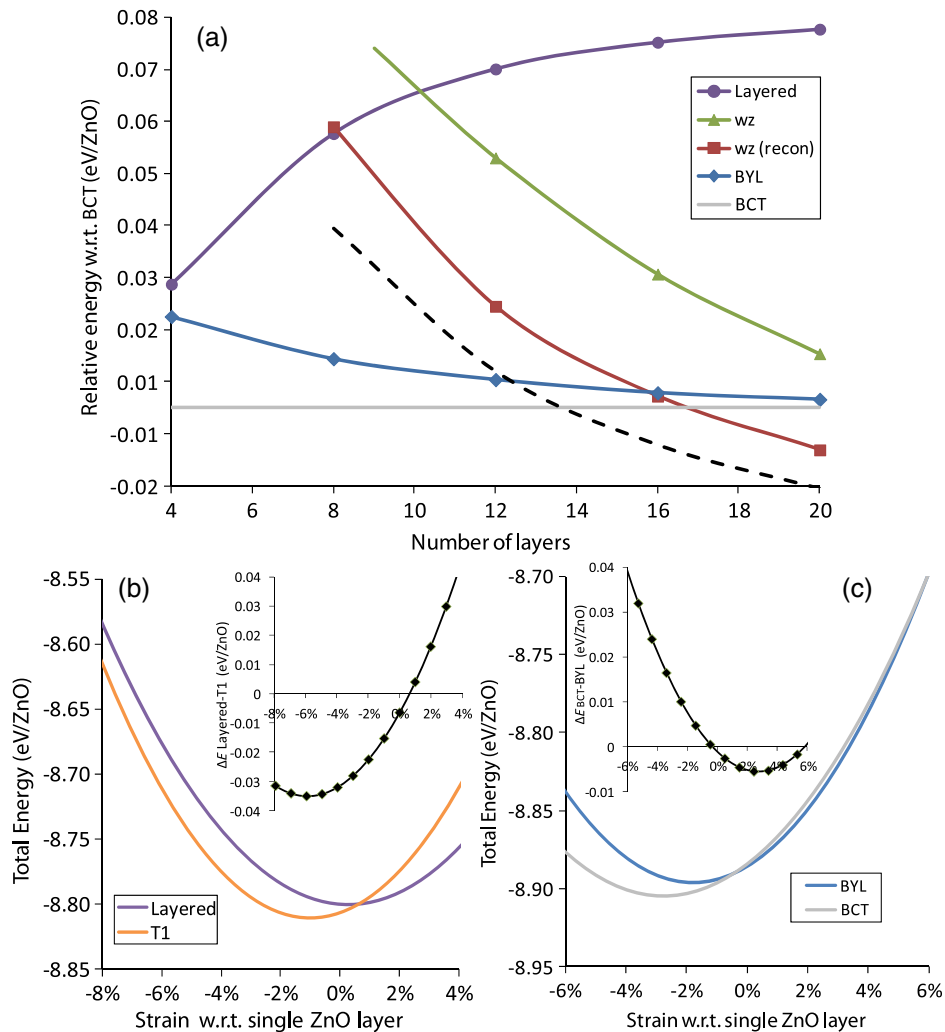

FIG. 3 (color online).   (a) Selected nanofilm energetic stability variation with thickness, (b) energy variation with in-plane strain for 4 ML layered-ZnO versus T1-ZnO, (c) energy variation with in-plane strain for 8 ML BCT-ZnO versus BYL-ZnO. Strains are relative to 1 ML layered-ZnO. Insets show polymorph energy differences.

wz-ZnO should be always more stable than unreconstructed wz-ZnO. We note that the individual ion transfer method has been estimated to be 0.3 eV less efficient per transferred ion than more sophisticated atomic reconstructions [25]. In Fig. 3(a) a dashed line shows the estimated downward shift due to such an improved model that has the main effect of causing the crossover with BCT-ZnO to occur at >14 ML rather than >16 ML.

Finally, we consider the effect of uniform in-plane $a - b$ strain on relative nanofilm polymorphic stability. We examine two systems: (i) T1-ZnO versus layered-ZnO in 4 ML nanofilms, and (ii) BYL-ZnO versus BCT-ZnO in 8 ML nanofilms. In the first case, as the two polymorphs are compatible with growth on metal (111) substrates, our calculations indirectly investigate the possible effect of epitaxy on nanofilm polymorphism. In a similar study in Ref. [5] only unreconstructed 4 ML wz-ZnO was used as a comparison with 4 ML layered-ZnO and thus the latter was proposed to be the most stable nanofilm structure for all strains. In Fig. 3(b) it can be seen that, although layered-ZnO is favored for larger positive strains, for small positive strains through to moderately compressive strains T1-ZnO is favored energetically. Our results imply that substrates with in-plane lattice mismatches that induce small compressive epitaxial strains could help to stabilize T1-ZnO. In the second case we investigate the role of strain in potentially altering the energetic ordering of low energy free-standing BYL-ZnO 8 ML nanofilms relative to BCT-ZnO. For 8 ML nanofilms reconstructed wz-ZnO is not energetically competitive with BCT-ZnO or BYL-ZnO but the latter two phases are close in energy. Under small positive strains we find that there is a small window of excess stability for the BYL-ZnO phase where energetic stability of the two nanofilms is inverted [see Fig. 3(c)]. These results further confirm other theoretical studies which suggest that mechanical forces applied to ZnO nanosystems may be a fertile route to access new polymorphs [6,11].

In summary, we have developed a method to generate a wide range of new low energy nanofilm and bulk polymorphs using nets as a basis. Consideration of the energetics of these structures permits an unprecendented overview of nanoscale polymorphism in ZnO and its evolution with size and strain. Our results provide convincing evidence that low energy polymorphism in nanofilms of wurtzite materials should be very rich, and significantly beyond the handful of polymorphs previous considered in the literature. Our results strongly suggest that many new nanofilm polymorphs should be experimentally accessible, and in some cases (e.g., T1-ZnO), may have even already been observed.

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