REVIEWS

Theoretical and Computational Studies of Nano-structures and Nano-materials

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Abstract | Theoretical analysis and computer simulations have proven to be cost-effective and powerful tools in scientific studies of materials, particularly at nano-scale where synthesis of nano-structures, interpretation of their observed character and exploration of new structures are not always straightforward. We present here fundamental principles of techniques used today for computational simulations of materials, their capabilities and limitations. We then illustrate efficacy of such studies through review of their applications to nano-structures of oxide materials, carbon and boron nitride based nano-tubes and mechanical behavior of nano-structured materials. We finally present a wish-list of new tools and augmentation of existing tools that would allow expansion of the range of applications of computer simulations to nano-structures and materials.

1. Introduction

With about a hundred elements in the periodic table as building blocks, there exist a very large number of materials that can be synthesized with different combination of these elements in different proportions. Interestingly, the structure of a material may not be unique, as different physical conditions or growth routes can trap a material in different meta-stable states. Properties of a material, which are completely determined by the chemistry and its structure, exhibit tremendous diversity. While it is fundamentally interesting how some of the properties can be classified into different universality classes, it is intriguing how the properties can change drastically with a slight change in chemistry or structure. A simple and commonly known example is of silicon versus carbon. While they belong to the same group of the periodic table and exhibit similar chemical bonding when in the same structure, the known ground state structures of silicon and carbon are diamond and graphite.

While silicon in diamond structure is one of the most important semi-conducting materials, and carbon (diamond) is the hardest and relatively rare material. Interestingly, the structural forms of carbon known recently, such as fullerene, nano-tube, graphene exhibit yet newer set of properties. The diversity in the materials world is what determines which material can be used in which applications, and understanding its origin is interesting and crucial to design of newer materials for technological applications.

At the nano-scale, there are at least two fundamental ways in which the diversity in the properties of materials becomes richer and interesting: (a) structure of a *bulk* material can be altered at nano-scale[1] (length-scale greater than the crystalline unit cells) and result in different properties (for example, mechanical behavior of nano-structured or nano-grained metal), and (b) a *nano-structure* has a large fraction of atoms at the surface (or interface) whose chemistry can

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be different from the atoms belonging to the bulk, hence possesses very different properties[2,3]. Experimental control and investigation of the structure and properties of nano-structures can be quite difficult and expensive. Measured properties of a nano-structure sensitively depend on how the experimental probe interfaces with the nano-structure mechanically, electrically or chemically. This necessitates use of tools that are complementary in their capabilities.

Advances in the hardware of computing resources and development of algorithms over the last few decades have resulted in computational methodologies that provide a powerful and independent approach to the exploration of materials, particularly at nano-scale[4]. Ideally, the computational approach to materials science has three goals: (a) understand the stability and mechanisms of properties of known materials, (b) complement experimental techniques by accessing information that is hard to determine unambiguously, (c) design novel materials and nano-structures. Such an approach has to capture both universality and diversity in the properties of materials and often has to start at the description of electronic motion in a material, with only input about the number and type of atoms constituting a given system, and is called as *first-principles* approach. Most commonly used first-principles methods[5] today are based on density functional theory (DFT) developed by Kohn and others in 1964–5[6].

From 1960's to 1990, many efforts were devoted to development of formalisms and concepts, which include (a) pseudopotentials and related schemes to describe effective potential of the atomic nucleus and core electrons, (b) Car-Parrinello molecular dynamics for thermodynamic simulations, (c) variational and iterative schemes for solutions of ground state and density functional perturbation theory, (d) "GW" approximation for estimation of energies of electronic excitations see Ref. 5 and references therein. Since early 90's, first-principles calculations have been used in ever expanding range of applications [witnessed by a Nobel prize in Chemistry for Walter Kohn in 1999]. Parallel to this in the 90's, efforts were devoted to (a) improving efficiency and scaling of first-principles calculations with size of the problem, (b) feeding the outcome of such calculations into models for larger-scale simulations. Rapid growth in research in nano-science instigated by the discovery of carbon nanotubes in early 90s and its need for simulation techniques have fuelled both further development of tools in computational materials science and their applications.

Nano-structures are also known as low-dimensional systems: dimensionality d of a nano-structure is the number of directions in which the size of a structure is greater than about 100 nanometers (along the remaining 3–d directions, the system is spatially confined). For example, the dimensionality of fullerene, nano-tube, graphene or epitaxial films is zero, one and two respectively. Due to confinement of quantum electronic states and deviation in the local coordination of atoms from that in the bulk, interesting quantum effects[7] and chemistry[3] emerge at nano-scale. Small changes in their structure can be introduced through doping or the strain constraints (as present in epitaxial films) at their interface with surrounding, which result in large and often qualitative changes in their properties. While advances in various electron microscopies have made it possible to image these structures at atomic resolution, their interpretation is often tricky and needs another "eye" for confirmation, which is often provided by first-principles computational tools. The doping of nano-structures, strain engineering of films, their hetero-structures can be exploited to design novel nano-materials through computer modeling alone.

Recent development in computing hardware has been towards *high-performance computing* (HPC)[8], which is characterized by a large number of small computers networked together through a fast and efficient architecture of network switch: a parallel computer cluster. Another related concept is of the *grid-computing*[9], in which computers across a network (not necessarily very fast) with idle cpu cycles can be utilized for simulations. Optimal use of such resources involves breaking of a computing problem and data into small bits that can be distributed over the large number of small computers (nodes) in the cluster. This naturally depends on the numerical representation of a problem and the extent of communication required between the nodes during computation. A class of problems involving large number of small tasks with minimal amount of inter-node communication is called as a *naturally parallel* problem. Design of materials with a given combination of elements is one such a problem where studies of different possible structures or materials can be distributed across different computing nodes.

In spite of availability of very large and powerful computers, many important problems in materials science are too large to be solved through simulations. Secondly, a large amount of data generated in large-scale simulations can be quite hard to learn fundamentals from. Modeling plays an important role in such problems which enables efficient solution of a problem and extraction of its

essential mechanisms. Modeling typically makes use of symmetries in integrating out irrelevant high energy degrees of freedom of a system. In any case, a computer-based solution of a challenging problem in materials usually involves a judicious choice of numerical accuracy and computational costs: higher the accuracy, greater is the cost!

In this article, we review in section 2 the principles fundamental to most computational techniques in materials science, and illustrate their applications in section 3 to some select problems in nano-materials based on mostly the author's earlier work, and summarize in section 4.

2. Basic principles

2.1. *Constitutive Energy function*

Total energy of a collection of atoms as a function of atomic numbers (type—chemistry) and positions (structure) of atoms $E_{\text{tot}}(Z_I, R_I)$ is central to most computational techniques in materials that *do not* aim at the detailed electronic structure and excitation properties of a system. Born–Oppenheimer (BO) approximation[10] is implicit in such techniques, which leads to separation between fast electronic degrees of freedom and relatively slower nuclear ones. The former are restricted in this approximation in their quantum mechanical ground state and the time evolution of the latter (except for very light elements like hydrogen) can be treated classically. The BO approximation breaks down when quantum ground and first excited states of electrons cross as the nuclear degrees of freedom evolve.

$E_{\text{tot}}(Z_I, R_I)$ contains all the material-specific details necessary to determine its properties. Minimization of E_{tot} with respect to $\{R_I\}$ results in determination of the theoretical structure of a system. The symmetry of the system which controls its universal properties is evident in the Taylor expansion of the total energy function at the theoretical structure:

$$E_{\text{tot}} = E_{\text{tot}}(\{R_I^o\}) + \sum_I \left.\frac{\partial E_{\text{tot}}}{\partial R_I}\right|_{R_I^0}(R_I - R_I^0) +$$

$$\sum_{I,J} \left.\frac{\partial^2 E_{\text{tot}}}{\partial R_J \partial R_I}\right|_{R_I^0}(R_I - R_I^0)(R_J - R_J^0) + \cdots$$

At the minimum energy or the theoretical structure, the first-derivative term in this equation vanishes, and the second derivative of energy with respect to R_I's is the force constant matrix, which yields vibrational frequencies through use of appropriate masses. Various derivatives of the energy function give various measurable properties of the system: first derivative of energy with respect to atomic

position, electric field, magnetic field and strain are the forces on atoms, electric polarization, magnetization and elastic stress of the system. Similarly, second derivatives with respect to electric field, magnetic field, and strain give the dielectric, magnetic and elastic compliances[11,12]. Mixed derivative give piezoelectric, piezomagnetic and magneto-electric response compliances[11,12]. Higher derivatives of the total energy are related to higher order (nonlinear) responses of the system[12]. The fact that energy of a system should be invariant under the application of a symmetry operation of the system, imposes constraints on various derivatives of energy, hence on the measured properties.

While the above analysis applies at zero temperature, it readily generalizes to finite temperature T through calculations of the free energy[13] $F = -k_B T \ln Z$, where the partition function Z is determined from the total energy function:

$$Z = \int \prod_{R_I} dR_I \exp\left(-\frac{E_{\text{tot}}}{k_B T}\right).$$

Relationships between derivatives of the total energy with observed properties translate to finite temperature through the derivatives of free energy. Evaluation of the partition function, however, is a difficult task as it involves a very large dimensional integral. In practice, it is accomplished through use of methods such as Monte Carlo and Molecular Dynamics (MD) simulations[14]. While the former use only the total energy function, the latter use energies as we as forces on the atoms given by the first derivatives. Such simulations typically are suitable to obtain free energy differences and not absolute values of the free energy. Estimates of some contributions to absolute free energy can be obtained through use of simple ideas such as the quasi-harmonic approximation or the Site-Occupancy-Disoder techniques[15].

Thus, it should be clear now that the accurate estimation of the total energy is crucial to determination of many properties of materials.

2.2. *Classical versus Quantum/first-principles approaches*

There are broadly two methodologies that allow access to the total energy function: (a) empirical ones in which a form of the total energy function is assumed with system-specific parameters values of which are obtained through fitting the energy function and/or its derivatives for certain relevant configurations to experimentally observed values, for example, the Stillinger–Weber potential[16] of silicon, (b) first-principles approaches[17,18] which

assume no experimental inputs and start with only the atomic numbers and possible positions as the specification of the system, arriving at material-specific total energy function. They necessarily make use of an approximate solution of the quantum mechanical equation of motion of electrons and include detailed chemistry of a material in mostly parameter-free way, which allows them to access material-specific properties.

Empirical approaches are usually very efficient (they are relatively expensive when long-range interactions are crucial to the properties of a material, such as ionic insulator, when the computer time of these calculations scales as square of the system size) and highly accurate in estimation of properties that are closely related to the observables used in fitting these functions[19]. In contrast, first-principles methods are usually very intensive computationally (computer time taken for these calculations scale as cube of the system size) and are reasonably accurate in most properties of the system. The biggest limitation of empirical approaches is that they can be developed practically for relatively simple systems and that their predictability is limited in terms of chemically as well as structurally new materials. Access to electronic details and chemical bonding of a system render additional advantage to first-principles methods.

Solution of a quantum many-electron problem is very difficult and is possible in numerically exact form with a quantum Monte Carlo method. However, quantum MC is computationally very intensive and at present can be used only for systems with a very small number of electrons. Most commonly used first-principles calculations today are based on density functional theory (DFT), in which the quantum many electron problem is mapped onto an effective single electron problem with a potential arising from electrostatic interaction with nuclei and other electrons, and exchange correlation interactions of electrons. The exact form of the latter is unknown and is approximated through its local dependence on electron density (local density approximation, LDA). This approximation is responsible for most limitations of a DFT-based determination of the ground state properties. Notably, DFT fails in materials where electrons are correlated, i.e. motion of an electron can not be treated effectively using the mean potential arising from other electrons. For simple systems, DFT-LDA based description of materials results in 2% underestimation of bond-lengths, about 10% errors in compliances such as bulk modulus with respect to experimental values.

There also exist semi-empirical approaches which aim at combining strengths of both of these methodologies.

2.3. *Effective Hamiltonians and Related Methods*

There are many problems in materials at nano-scale which can not be tackled realistically through *direct* use of first-principles simulations, because of the computational resources and time needed for completion. There are broadly three strategies one can follow in such cases: (a) construction of effective Hamiltonian through identification of the symmetry-invariant subspace of low energy degrees of freedom and projection of the full Hamiltonian into this subspace using an appropriate basis, which can be used in large-scale simulations, (b) use of first-principles methodology in a sub-domain embedded in a region treated with classical (for example, continuum) energy function obtained as an appropriate limit of first-principles total energy function, for example, the quasi-continuum methodology[20], (c) use of phenomenological models or theories whose parameters are determined from first-principles calculations; this approach is useful where neither (a) nor (b) can be used effectively.

3. Applications To Nano-structures and Nano-materials

While the structure of a system can be theoretically determined through minimization of the total energy function, it is often a very hard task. The cause of this difficulty lies in the fact that the total energy function can be a highly nonlinear function of atomic positions with several possible local minima. Most methods of minimization of a function typically start with an initial guess for a minimizing vector (structure) and iteratively determine the minimum of function in the same basin. The phase space of structures grows exponentially and search through all possible basins of energy function to determine its global minimum is a task that can not be solved using the known computing concepts in time that scales as a polynomial of the system size. Genetic algorithm provides a popular option to try to find a global minimum. In the context of structural optimization of nano-clusters, we presented an algorithm that was based on physical intuition and symmetry[21]. Our approach is based on the use of Hessian, the second derivative matrix of the total energy (with respect to atomic positions), in addition to the energy and forces. Eigenvalues of this Hessian relate to vibrational spectrum of a system, and the modes with imaginary frequencies specify the directions in the structural space along which the structure is *unstable*, i.e. it would distort to a lower energy structure. An intuitive assumption in our approach is that the basins of the energy function can be "accessible" from *a* high symmetry structure and

that different basins can be spanned by considering various high symmetry structures for clusters of a given size. In summary, the approach considers as many high symmetry structures (which are relatively smaller in number and easier to generate) of the given size cluster as possible. For each such a structure, it finds the Hessian matrix (this is readily accomplished through DFT linear response calculations) and distorts the structure with the strongest instability, and subsequently uses the standard algorithms to find the local minimum of energy. In the course, this scheme generates many structures corresponding to local energy minima along with their vibrational spectrum, which are relevant to finite temperature analysis. This was shown to be successful in predicting the structure of Sn_{13} cluster that is lower than most known structures of Sn_{13}.

The level of difficulty in determination of structures reduces as one goes to structures with higher dimensionality (clusters are *zero* dimensional nano-objects) and regularity/periodicity along the extended dimension. For example, the structure of a nano-wire or a nano-tube is determined with fewer parameters even though number of atoms in it can be large. We review here now computational studies of nano-structures in 2 and 1 dimensions, whose structure is relatively simpler to determine and properties can be quite interesting.

3.1. Two-dimensional Nanostructures of Ferroelectric Oxides

Miniaturization of devices and development of chips with a very high density of devices have been central to technological evolution over the last several decades. Ferroelectric or piezoelectric oxides, also known as *smart* and functional materials, are essential to the Micro-Electro-Mechanical-Systems (MEMS), which are used in a very wide range of applications ranging from ultra-sound detectors in a hospital to the ones on submarine. Ferroelectric oxides possess spontaneous (in the absence of field) electric dipole or polarization that couples strongly with strain, which allows them to be used as sensors as well as actuators of mechanical strain. Since this spontaneous polarization can be *switched* to other directions with applied electric field, they can also be used in non-volatile memories (known as FeRAMs). Scaling down of MEMS or FeRAMS to nano-scale (NEMS) depend crucially on how properties of a ferroelectric films change when the film thickness shrinks to less than nano-meter.

Fundamentally, the question of existence of polarization in nano-thin films of ferroelectrics is also related to probing how the ferroelectric phase transitions occur when a material is confined to less than 100 nm along one of the directions. In our work, we have combined investigation of this with the search for lead-free ferroelectrics. While the development of lead-free ferroelectrics is essential to environment-friendly technologies, it is also chemically interesting and challenging to find alternative routes to develop better ferroelectrics *with out* the stereochemically active lone pair chemistry of lead. Here, we review our work that tries to make use of tunability at nano-scale of two types: (a) strain engineering of epitaxial films of $BaTiO_3$,[22] and (b) artificial superlattices of $BaTiO_3/SrTiO_3$ (BTO/STO)[23].

3.1.1. Ultra-thin films of BaTiO₃

The structure of a film of an oxide (or other materials) is determined by the competition between (a) the energy of the interface with substrate on which it is grown, which is most stable then the film and the substrate are perfectly in registry, i.e. have the same in-plane lattice constant, and (b) the elastic energy associated with strain in the film that may be present to match its lattice constant with the substrate. For films thicker than a critical thickness, the elastic energy cost (which scales with volume) dominates, and the film has a structure essentially the same as of its bulk form. As a result, there can be dislocation or other extended defects at the interface. For thinner films, the interface energy is dominant and the film has the same in-plane lattice constant as of the substrate (and often different from its bulk form). Such a a strain in the film induced by the substrate is called as epitaxial strain. As ferroelectrics exhibit a strong coupling between polarization and strain, epitaxial strain can be used to engineer properties of ultra-thin ferroelectric films[24].

First-principles MD or MC simulations of ferroelectric films (eg. $BaTiO_3$) are presently not feasible as the size of systems necessary in a study of phase transitions is too large (more than a few thousand atoms). We used an effective Hamiltonian that is obtained in principle by projecting the complete lattice dynamical (phonons). Hamiltonian into the subspace spanned by phonon bands of the cubic structure which include unstable optical modes and acoustic modes using phonon Wannier functions as a localized basis. The form of the model is naturally determined by the symmetry-invariant Taylor expansion of the total energy function in terms of Wannier or local modes, containing anharmonicity of optical phonons and their coupling with strain, elastic energy associated with homogeneous strain, and acoustic modes within harmonic description. The effective Hamiltonian thus consists of two classical vector

Figure 1: Ferroelectric slab with electrodes modeled as electrostatic mirrors (a) perfect electrode (b) imperfect electrode. Arrows indicate local electric dipoles. While the electrostatic image of out-of-plane component of a dipole is parallel to that of the dipole, the image of the in-plane component is inverted.
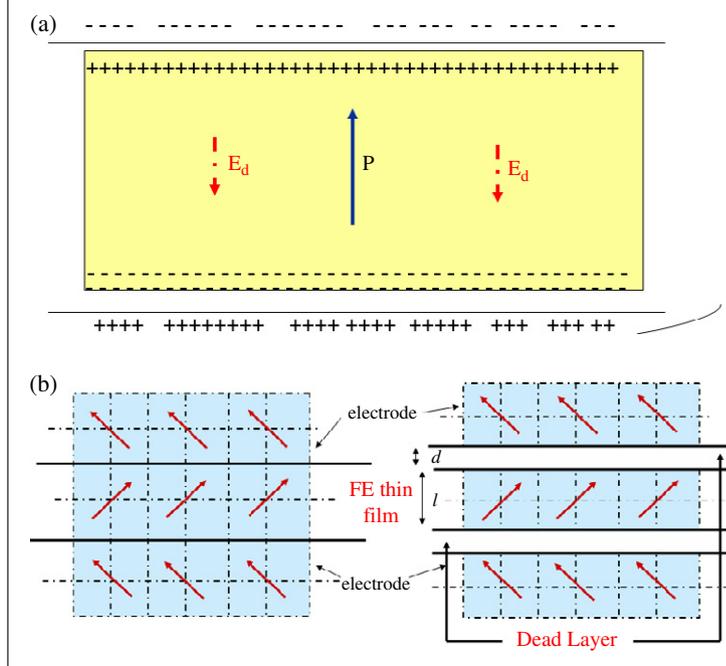
degrees of freedom per cell: one centered at Ba-site spans the acoustic phonons, and another centered at Ti-site spans the optical modes. The former captures the effects of inhomogeneous strain, and the latter correspond to the local electric dipoles. Simulations of such an effective Hamiltonian are still very demanding due to infinite range dipole–dipole interactions and we have developed a mixed space MD code[25], named as FERAM[26].

As is known in other contexts such as conductivity of a nano-tube, properties of a nano-structure depend sensitively on the probes interfacing with it during a measurement. In the present case, the nature of the electrodes determines the electrical boundary conditions at the surface of the films (see Fig. 1a). If the electrodes are perfect metals, the bound surface charges of a ferroelectric are completely compensated by the free carriers of the electrode; imperfect electrodes result in partial compensation of these charges. The effects of electrodes have been captured with a simple model based on electrostatic mirrors and that contains a single length-scale: thickness d of a dead layer that separates electrodes and the ferroelectric slabs (see Fig. 1b). Perfect electrodes correspond to the thickness d of zero, and imperfect electrodes are simulated with a nonzero d. In the case of former, the depolarization field associated with bound

surface charges is zero, where as in the latter, it is proportional to $d/(l+d)$, l being the thickness of the film. When $d = 0$, or a, the lattice constant, it can be shown that overall system consisting of dipoles in the ferroelectric slab and their images in electrodes form a periodic system with periodicity of $2(l+d)$ along z-axis.

Epitaxial strain constraint is imposed by fixing the in-plane components of the homogeneous strain. Polarization, calculated as a thermal average of spatially averaged local electrical dipoles of the system, is the order parameter of ferroelectric phase transitions. Polarization along [001], [110] and [111] directions correspond to tetragonal, orthorhombic and rhombohedral ferroelectric phases respectively. Extensive MD simulations of $BaTiO_3$ sandwiched between perfect electrodes, at different epitaxial strains and temperatures, were used to generate temperature–strain phase diagrams (see Fig. 2a). Ferroelectric transition temperature can be enhanced by almost a factor of two (with respect to bulk) by imposing compressive epitaxial strain. As the strain becomes tensile, there is a transformation from tetragonal to monoclinic to orthorhombic phases, with rhombohedral phase stabilized only at a specific value of strain. Such phase diagrams should be useful in design of devices based on epitaxial ferroelectric films.

Figure 2: (a) Temperature-epitaxial strain phase diagram of BaTiO₃ slab with perfect electrodes, (b) A horizontal planar section of the low temperature phase of a ferroelectric slab sandwiched between imperfect electrodes, exhibiting striped domains polarization (blue region denotes up polarization and red region down polarization).
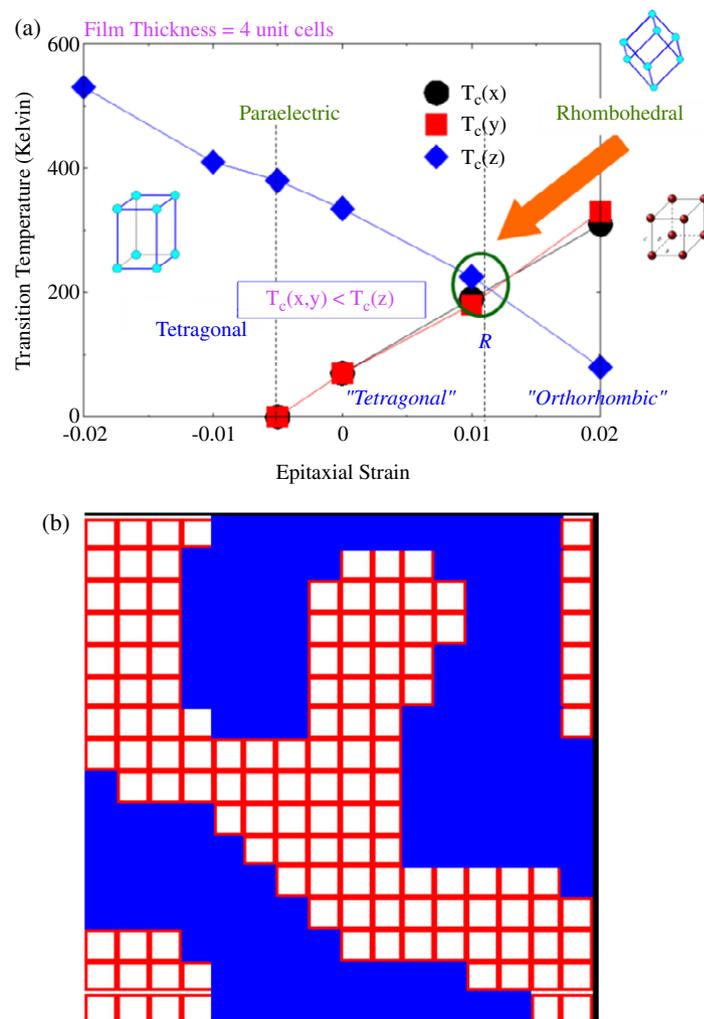
Effect of electrodes on the nature of ferroelectric phase is rather striking. For ultra-thin films, when the depolarization fields are not adequately screened by the limited free carriers in "imperfect" electrodes, the low temperature phase develops stripe-like domains of polarization. Extensive simulations of this phase showed that the periodicity length-scale of the stripes varies as square root of the thickness of the film[25]. These simulations have confirmed experimental observation of striped phases[24] and traced their origin to the nature of electrodes.

3.1.2. *Artificial Superlattices of BTO/STO*

Advances in epitaxial engineering have made it possible now the atomic layer-by-layer growth of oxides films. Different atomic planes can

alternate or be grown with different periodicity thus forming superlattices. For example, a 1:1 BTO/STO superlattice is formed when a layer of BaTiO₃ and a layer of SrTiO₃ alternate (see Fig. 3a). This allows control over both structure and chemistry of oxides at nano-scale in being able to tune their properties. Superlattices open up possibilities of new kind of functionalities arising from the combination of properties of its constituents as well as from the interface between the them. While growth of superlattices is possible, it needs advanced technologies and is expensive, as there are many possibilities to explore. First-principles simulations have proven to be cost-effective and reliable tools in investigation of such superlattices.

Superlattices of BaTiO₃ and SrTiO₃ have been of interest due to (a) moderate lattice mismatch

Figure 3: (a) BTO/STO superlattice, and (b) its polarization as a function of epitaxial strain.


(a)

Sr
Ba
Ti
O

[001]

[100]

(b)
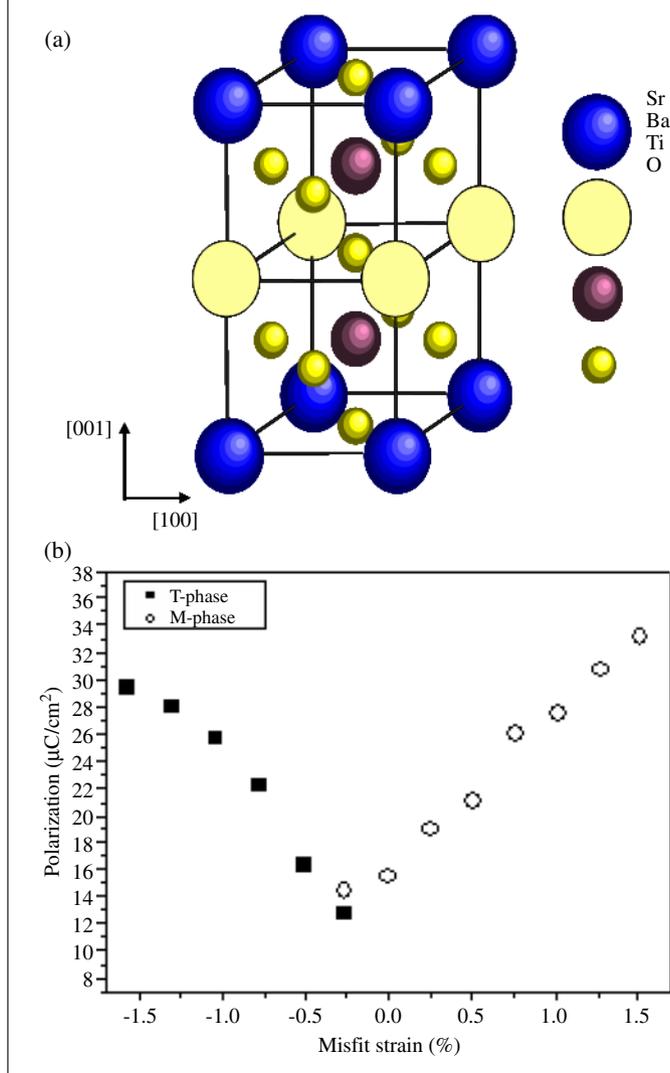
between the two, (b) the fact that BTO is a ferroelectric while STO is a quantum paraelectric, and (c) the resulting ferroelectric would be lead-free. Our first-principles simulations of the BTO:STO superlattices[23] have shown how sensitively its structure and polarization depend on epitaxial strain. Starting with a tetragonal phase with a very large polarization at compressive strain, the 1:1 BTO:STO superlattice transforms to a monoclinic phase at the epitaxial strain of −0.25%. Magnitude of the polarization in monoclinic phase grows with tensile strain. Along this transition as a function of strain, polarization vector essentially rotates in xz-plane. Most materials exhibit anomalously large response properties. BTO:STO superlattices exhibit a very large dielectric response near the epitaxial strain of −0.25%, arising from one of its TO phonon with z-polarization that becomes soft.

3.2. One-dimensional Nanostructures: BC_4N nano-tubes

Among all the known nano-structures, carbon nano-tubes (CNT) have attracted a great deal of attention and research activities[27]. CNTs have extraordinary mechanical stiffness and their electronic properties sensitively depend on the chirality (i.e. their structure). CNTs are labeled with integer chirality indices (n, m) which specify the lattice vector of graphene lattice along which graphene is rolled to form the nano-tube. CNTs can be metallic as well as semiconducting depending on their chirality: CNTs with integer value of $(n - m)/3$ are metallic and the rest are semiconducting. While these properties make CNTs very interesting and useful in applications, there is no method as of now that allows separation of CNTs into metallic and semiconducting types[27].

Figure 4: A junction between (6,6) boron nitride and carbon nano-tubes.
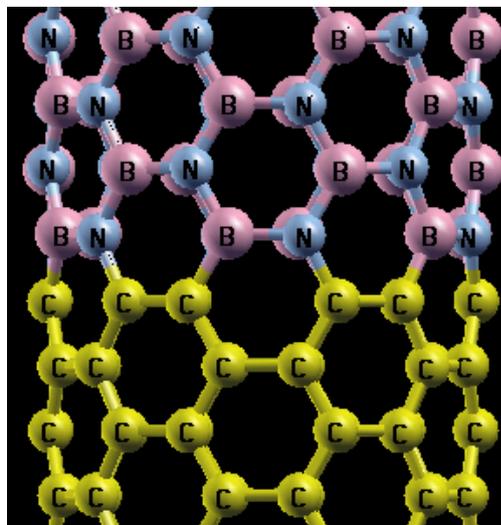
Boron nitride nanotubes (BNNTs), while structurally similar to CNTs, are all insulating due to partial ionic nature of B and N. Doping BNNTs, for example with carbon, can help in making them semi-conducting: carbon substitution at B and N sites make them n-type and p-type semiconductors respectively. However, the effective mass of the carriers still remains very high due to relatively flat electronic bands in the gap arising from dopants. Similarly, doping of CNTs with B and N allows tuning of their electronic structure near the Fermi level[28].

Taking these ideas further, CNR Rao et al[29] synthesized nano-tubes that are sort-of solutions of CNTs and BNNTs with 2:1 proportion. Interestingly, the resulting BC_4N nano-tubes of $(6, 6)$ chirality, where the host $(6, 6)$ CNTs are metallic, exhibited insulating behavior. This puzzling experimental observation was complemented with our first-principles calculations. Our calculations showed that the electronic structure of BC_4N nano-tubes is very sensitive to the way in which B and N decorate (or distribute on) the CNT lattice. We considered to different configurations: (a) pseudo-random distribution of B and N, (b) configurations with a pair of C–C atoms in each hexagonal ring replaced with B–N, (c) CNT with BN_3 and NB_3 local structures randomly distributed, and (d) CNT with BN_3 and NB_3 local structures linked with a B-N bond. Our simulations singled out the configuration (d) as the lowest energy configuration and also showed that this was the only configuration exhibiting insulating electronic properties. Thus,

our calculations not only complemented the experiments by determining a detailed structure of BC_4N nano-tubes, but also helped in understanding its link with electronic properties.

Our results for energetics of B and N distribution on a CNT revealed that there is a good probability that BNNT and CNT may phase-separate. This allows us to predict a stable junction between BNNT and CNT of identical chirality (see Fig. 4). This junction or a one-dimensional hetero-structure (for (6,6) chirality) is an insulator-metal junction that can be exploited in ultra high frequency diode-based device applications.

3.3. *Mechanical Behavior of Nano-structured Mg–Zn–Y alloys*

Bulk materials with nano-scale structure, for example consisting of nano-sized (<100 nm) grains, often exhibit a very high mechanical strength[30]. Such materials, have a large fraction of atoms at the interfaces between grains. Due to different structural geometry and chemistry, this can qualitatively change their properties at different scales. Recently, addition of small amount of Y and Zn was reported to have improved strength of Mg and also incorporate creep resistance at high temperatures[31]. The origin of these interesting properties was linked with nano-scale structure of these alloys—long periodic structures. While mechanical behavior of a material involves processes at different, particularly longer length scales, direct understanding of such phenomena from first-principles is really ambitious. While classical MD simulations[30] have proven to be very effective in assessing role of different mechanisms responsible for unique mechanical behavior of nano-structured materials, such methods fail to capture the effects of detailed chemistry. We used first-principles calculations to confirm the stability of long-periodic structures and evaluate their implications to mechanical behavior through phenomenological concepts such as stacking faults.

Outcome of first-principles calculations can be connected to mechanical behavior, even to brittleness versus ductility, through the concepts of (a) cleavage (or surface) energy, which is the energy required to separate away its two halves separated by a crystallographic plane or a grain boundary, and (b) generalized stacking fault energy surface, which is the energy required to slide a half of a crystal with respect to another. While the former relates to energy release rate required for crack propagation during brittle failure (Griffith criterion), the minima and maxima of the latter relate to intrinsic and unstable stacking fault energies (Rice theory).

Our simulations[32] of different polytypes of Mg revealed that the 6-layer structure of Mg is

remarkably stable, and only about 50 meV/atom higher in energy than the hcp structure. Origin of this could be traced through topological analysis of electron density to the similarity in bonding of 2-layer and 6-layer structures and finally to the close-packed nature of the two. Addition of small amount (2%) Y to Mg results in the l-layer structure lower in energy than the hcp structure. Through extensive stacking fault energy calculations, we found that energy of the stacking fault in the basal plane reduces dramatically with addition of Zn, and showed that 6-layer structure should exhibit activation of the slip on prismatic plane. These findings should be useful in understanding deformation mechanisms in these nano-structured alloys of Mg.

4. Summary

After a brief presentation of basic principles of the computational methods in materials science, we illustrated their impact in three different areas in nano-science through review of earlier works. We showed how these calculations complement experimental efforts in synthesis and characterization of novel nano-structures such as BC_4N nano-tubes. Secondly, we reviewed computational modeling and prediction of temperature strain phase diagram of ultra-thin epitaxial films of $BaTiO_3$ that would help in design of devices based on epitaxial films of oxides. Finally, we showed how these calculations can be used within simple phenomenological theories to connect with complex materials properties relevant to mechanical behavior, through an example of nano-structured Mg alloys.

There are certain limitations of the current methods in computational materials science particularly in view of their applications to nano-scale materials. Most of the first-principles codes[33–35] employ periodic boundary conditions, which are not quite suitable for low-dimensional systems such as nano-structures. This poses a particularly tricky problem while simulating *charged* nano-structures, for example doped graphene. It would be ideal to have a first-principles code that uses mixed boundary conditions, For example, a code that treats *d*-dimensions with periodic boundary conditions and 3–*d*-dimensions with open boundary conditions. Secondly, determination of properties that involve electronic excitations is not quite straight-forward and readily feasible. Another limitation of the existing methods lies in applications to dynamical quantum phenomena including transport of electrons through nano-structures. At present, theories and calculations based on simple model Hamiltonian have been used in understanding these phenomena, but studies

with accurate description of realistic electrodes and interfaces are still limited. While approaches based on time-dependent density functional theory have been implemented to tackle some of these issues, there still is room for developing innovative methods. Finally, multi-scale simulation methods (which employ different methodologies for different scales in the same simulation) are expected to have a great impact in biological as well as materials sciences at all scales. In these methods, there is still need to develop a clear formulation that allows use of a combination of quantum and classical analysis in spatially interfacing domains.

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