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Theoretical and Computational Studies of Nano-Structured Materials and its Commercial Prospects in India

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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 straight forward. 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 and mechanical behaviour of nano-structured materials. The area of nano-science and technology is growing rapidly around the world and nano-materials based products, especially in the consumer sector, are coming into market very rapidly. India is competing with great difficulty, with other developed countries to make its position strong in this field. In other respect, several challenges have to be overcome in terms of production of nano-materials at commercial scale, their processing, applications and commercialization.

I. INTRODUCTION

Nanotechnology, defined as the application of nano-science in technological devices/processes/products, is fast emerging as an important enabling technology capable of impacting almost all the sectors of industries and consumer products. Therefore, not surprisingly, all governments and industries the world over are investing heavily in the development of nano-technology based processes, products and systems. Nano-technology represents a very broad area and is composed of three main fields, i.e., nano-materials, nano-tools and nano-devices. Of these, both research and commercialization have occurred to a significant level only in the area of nano-materials. In India also much of the research and technology development work has taken place in the arena of nano-materials. Thus, this paper will concentrate on highlighting the status of nano-materials research and commercialization in India. Nano-materials represent a class of materials characterized by a feature size of less than 100nm. In the case of nano-particles, the feature size is the particle diameter while in carbon nano-tubes; it is the nano-tube diameter. At the other extreme, in the case of bulk materials, either the grain size in homogeneous materials or the reinforcing particle size and spacing in the case of composites represent the feature size. Thin films having thickness less than 100nm or multi-layer coatings with the thickness of each layer less than 100nm also qualify as nano-materials. Therefore, it is important to note that while nano devices will certainly have to be made from nano-materials, nano-materials itself impacts areas beyond nano-technology. For example, the recently developed nano-steel by a Japanese company [13] is a nano-material which will impact the automobile and infrastructure industry by providing high strength, high toughness steel sheets with superior formability and corrosion resistance. It is also important to understand that merely bringing the feature size to below 100nm is not enough; more importantly, such a decrease in feature size should result in significant enhancement of strength, toughness or electrical, electronic, optical and magnetic properties.

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 verses carbon. While they belong to the same group of the periodic table and exit similar chemical boding when in the same structure, the known ground state structures of silicon and carbon are diamond and graphite.

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[5] length-scale greater than the crystalline unit cells) and result in different properties (for example, mechanical behaviour of nano-structures or nano-grained metal) and

(b) A Nano-structure has a large fraction of atoms at the surface (or interface) whose chemistry can be different from the atoms belonging to the bulk, hence possesses very different properties. [6]

Experimental control and investigating of the structure and properties of nano-structures can be quite different 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.

Nano-structures are also known as low dimensional systems: dimensionality d of a nanostructure is the number of directions in which the size of a structure is greater than about 100nm (along the remaining 3-d directions, the system is spatially confined). Due to confinement of quantum electronic states and deviation in the local co-ordination of atoms from that in the bulk, interesting quantum effects and chemistry [6] 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. 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. Modelling plays an important role in such problems which enables efficient solution of a problem and extraction of its essential mechanisms. Modelling 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.

II. 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 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 the 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 cannot 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 [12]. 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 nao-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.

III. TWO DIMENSIONAL NANO-STRUCTURES OF FERRO-ELECTRIC 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. Ferro-electric or piezo-electric 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.

Ferro-electric 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 ferro-electric films change when the film thickness shrinks to less than nano-meter. Fundamentally, the question of existence of polarization in nano-thin films of ferro-electrics is also related to probing how the ferro-electric phase transitions occur when a material is confined to less than 100nm 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 ferro-electrics without the stereo-chemically active lone pair chemistry of lead. Here, we review our work that tries to make use of tenability at nano-scale of two types:

(a) Strain engineering of epitaxial films of BaTiO3 [8] and

(b) Artificial super lattices of BaTiO3/SrTiO3 (BTO/STO) [10].

IV. MECHANICAL BEHAVIOUR OF NANO-STRUCTURED MG-ZN-Y ALLOYS

Bulk materials with nano-scale structure for example consisting of nano-sized (<100nm) grains, often exhibit a very high mechanical strength. [7] 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 report to have improved strength of Mg and also incorporate creep resistance at high temperatures [2]. The origin of these interesting properties was linked with nano-scale structure of these alloys long periodic structures. While mechanical behaviour 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 [7] have proven to be very effective in assessing role of different mechanisms responsible for unique mechanical behaviour 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 behaviour through phenomenological concepts such as stacking faults.

Outcome of first principles calculations can be connected to mechanical behaviour, 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 [1] of different polytypes of Mg revealed that the 6-layer structures of Mg are 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 bending of 2-layer and 6-laye structures and finally to the close-packed nature of the two. Addition of small amount (2%) Y to Mg results in the 1-layer structure lower in energy then the hcp structure. Through extensive 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.

V. INDIAN SCENARIO

(a) Government Support: Compared to developed countries, India has initiated a focused effort on nano-technology only in 2001, i.e. 5-7 years after countries like USA, EU, Japan, Korea and Tiwan started their own programmes. In October 2001, India launch a major programme in nano-technology when Development of science and technology(DST) launched the nano-science and technology Initiative(NSTI) and operated it for 5 years during the period 2001-02 to 2006-07. During this phase, the emphasis was on creating centres of Excellence in various aspects of nano-technology in the various universities and R & D laboratories in India. Bulk of the funding was utilized to procure specialized equipment required for nano-science like AFM, SEM, TEM, Nanoindentor etc. In all, about 100 projects were funded under NSTI.

Enthused by the over whelming response to the NSTI programme, DST has now initiated the Nano-Mission programme with a funding of Rs.1,000 crores over the period 2007-08 to 2001-12[16]. However, unlike NSTI, Nano Mission has created three full fledged institutions of Nano-science and Nano-technology in Bangalore,Kolkata and Mohali respectively. Further, the Nano-Mission will not only support high quality research in nano-science(as NSTI did earlier) but also fund projects focussing on application and product development with the active participation of Indian industries. It should also be pointed out that other governmental agencies like CSIR, DBT, DRDO, DAE and ISRO are also undertaking major projects in the area of nano-science and nano-technology.

(b) Industrial Support to Nanomaterials: Unlike in USA, Europe and Japan, the Indian industries have started looking at nano-technology as a solution for their problems only recently. Among the bigger companies, Reliance Industries, Tata Chemicals, Mahindra and Mahindra, Ashoke Leyland, Asian Paints, Crompton Greaves have initiated programmes in the area of nano-materials on their own or in collaboration with academic/R & D institutions. In addition, industry associations like Confederation of Indian Industry (CII), Federation of Indian Chambers of Commerce and Industry (FICCI), Society for Indian automobile Manufacturers (SIAM), Automotive Component Manufacturers Association (ACMA) have realized the importance of nanomaterials and nanotechnology and have started arranging get together among the industry representatives and experts in nano-materials/nanotechnology to evaluate the possibilities with respect to nano-materials in the industry.

(c) Nanomaterials: Commercialisation: The migration of the technology developed at the laboratory to the market place is more challenging than the development of the technology itself. Apart from the scalability and cost-effectiveness of the process/technology to enable large-scale production, it is important to ensure that sufficient market (new or replacement) is available for the product produced using the process/technology. Even if sufficient market is waiting to be tapped, marketing skill largely determines the actual market size for the product.

The ARCI technology for nanosilver based candle filter has been transferred to SBP Aquatech Pvt. Ltd., a Hyderabad company, which will have an initial capacity to product 500 candles a day [18]. The product, already in the market (fig1) is now undergoing initial marketing trials.

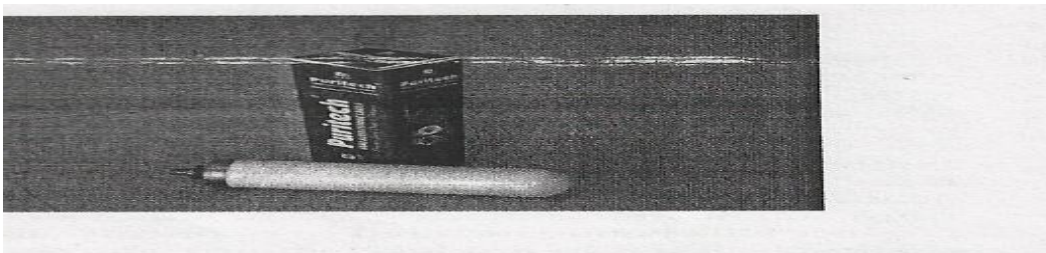

Fig1: Commercial nanosilver-coated ceramic candle filters for drinking water. (technology developed and transferred by ARCI)

Like the Hyderabad Company marketing nanosilver candle filters, there are a few more companies operating in the area of nano-materials and all of them are operating at small scales. For example, United Nanotechnology products, Kolkata has set up a pilot scale production facility for nanocrystalline Lithium iron phosphate required for making the electrode for Li-ion batteries [19]. However, the above product is largely meant for export. Similarly, Monad Nanotech Ltd. And Innovation Unifed Technologies, both from Mumbai, are selling carbon nanotubes and carbon nanofibres, but in small quantities.

(d) Safety, Health and Environmental (SHE) Issues: It is increasingly becoming apparent that nanotechnology, though touted as the future solution for almost all our technological requirements, has to be assessed carefully and now with regard to safety, health and environmental (SHE) issues so that we do not repeat the mistakes made in the past with regard to asbestos, chlorofluorocarbons etc. The technology community should evaluate the SHE issues with an open mind, on the basis of scientific data, and voluntarily embark on regulatory measures and create specific standards for nanotechnology products. In extreme cases, wherein the health, safety or environmental concerns are sufficiently high, the concerned product/technology should be abandoned or temporarily suspended till specific evaluation studies are carried out to resolve the issue.

VI. NANOMATERIALS: APPLICATION DEVELOPMENT

As India is already behind the developed countries in both nano research and application development by 5-10 years, it is important that India chooses the application areas for nano-materials wherein either the Indian market is very large in the world context or which are unique/specific to India. Examples of the former include two and three wheelers, auto component and textiles markets while the health, drinking water are examples of the latter. The application-oriented research in India in the last few years has focused primarily on energy, environment and health related areas. For example, the invention of flow induced electrical response in carbon nano-tubes has direct relevance in biological and biomedical applications [14]. Indian Institute of Science has transferred the exclusive rights of this technology to an American start-up to commercialize the gas-flow sensors. Nanocrystalline gold triangles developed by a group at National Chemical Laboratory (NLC) have been shown to be useful for cancer treatment by hyperthermia, where the irradiation of the cancer cells is carried out by infra-red radiation [15].

Name	Type	Country	Products
Bayer	Big Chemical	Germany	Bulk production of Baytube carbon nanotubes
BASF	Big Chemical	Germany	Bulk production of various nanomaterials (Uses include food additives and sunscreen)
Degussa	Big Chemical	Germany	Bulk production of a range of ultrafine and nanomaterials
ICI/Uniquema	Big Chemical	UK	Bulk production of nanomaterials (including nano titanium dioxide for sunscreens)
Mitsubshi Chemical	Big Chemical	Japan	Bulk production of carbon nanotubes
Advanced Nanomaterials	Nano Specialist	Australia	Bulk production of a range of nanomaterials (Uses include sunscreens,catalysts, cosmetics and coatings)
Nanophase	Nano Specialist	USA	Bulk production of a range of nanomaterials
Hyperion Catalysis	Nano Specialist	USA	Nanotubes for incorporation into plastics
Carbon Nanotechnologies Inc	Nano Specialist	USA	Bulk production of carbon nanotubes
Umicore	Specialty Chemical	Belgium	Bulk production of nanomaterials (including nano titanium dioxide for sunscreens)
Elementis	Specialty Chemical	UK	Bulk production of nanomaterials (including nanoparticles ZnO sunscreens)
Nanogist	Nano Specialist	South Korea	Bulk production of nanomaterials (anti microbial silver nanoparticles)
Qinetiq Nanomaterials	Nano Specialist	UK	Bulk production of a range of nano- materials

Table1: Major global manufacturers of engineered nano materials

These materials have also found their use in insulin delivery for advanced diabetics. NCL has already applied for an American patent for this breakthrough. The achievements of a research group at University of Delhi on drug delivery are highly commendable. This group has developed 11 patentable technologies for improved drug delivery systems using nanoparticles. One of the important achievements of this research is the development of a reverse micelles based process for the synthesis of hydrogel nanoparticles for encapsulating water-soluble drugs. This technology has been sold to Dabur research foundation in India. They are also co-developing nano-polymer and liposome based drug delivery systems. A research group at Banaras Hindu University has developed a novel method to produce a membrane out of carbon nanotubes for treating contaminated drinking water [3]. Eureka Forbes, in collaboration with IIT Madras, has come out with a nanosilver-based water filter for the removal of dissolved pesticides in drinking water [4]. Among the Indian research laboratories, ARCI is one of the fast growing research centres with a unique mandate to develop and demonstrate technology and transfer the same to industries. ARCI has set up the Centre for Nanomaterials with a view to develop nanomaterial synthesis and application technologies which are scalable and economical in comparison to existing technologies.

VII. CONCLUSIONS

After a brief presentation of basic principles of the computational methods in materials science, we reviewed computational modelling 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.

Secondly, we showed how these calculations can be used within simple phenomenological theories to connect with complex materials properties relevant to mechanical behaviour, 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. Another limitation of the existing methods lies in applications to dynamical quantum phenomena including transport of electrons through nano-structures. 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 s materials sciences at all scales.

The awareness about nano-materials and nano-technology and its benefits to society has continuously increased among the Indian Scientific and Industrial Community over the last decade. The intensity of scientific research in the area has also increased considerably over the years; though in terms of number of quality publications in technical journals, we still lag behind countries like Korea, China and Taiwan leave alone the leading countries like USA, Japan and Europe. However, in the areas of application development and commercialization of nano-materials based technologies, India is far behind even compared to countries like Singapore.

REFERENCES

[1]. Datta, U V Waghmare, U Ramamurty, Actu Mat 56, 2531 (2008).
[2]. Abe E, Kawamura Y, Hayashi K, Inoue A, Actu Mater. 50, 3854 (2002).
[3]. Srivastava, O.N.Srivastava, S.Talapatra, R.Vajtai, P.M.Ajayan, Nature Materias, 3(2004)610.
[4]. S. Nair, T.T.Renjis and T.Pradeep, J.Environ.Monit, 5(2003)363.
[5]. Carl C. Koch, Nanostructured Materials: Processing, Properties and Applications, William Andrew Publishing; Enlarged 2nd edition (2006).
[6]. C.N.R.Rao, Achim Mullar, Anthony K. Chutham, Nanomaterials chemistry: Recent Developments and New Directions, Wiley-VCH; 1 edition (2007).
[7]. H.Van Saygenhoven, Materials science and Engineering A 483, 33(2008).
[8]. Jaita Paul, T.Nishimatsu, Y.Kawazoe and U.V.Waghmare, Phys.Rev.Lett.99, 077601(2007).
[9]. K.J.Choi et. al, Science 306, 1005 (2004).
[10]. L.Kim, J.Kim, D.Jung, J.C.Lee and U.V.Waghmare, Appl. Phys. Lett. 87, 052903(2005).
[11]. Michael Plischke and Birger Bergersen, Equilibrium Statistical Mechanics, World Scientific, 3rd Edition (2006).
[12]. R. Pushpa, S.Narasimhan and U.V.Waghmare, J.Chem.Phys.121, 5211(2004).
[13]. S.Tetsuo, F.Yoshimasa, K.Shinjiro, JEE Technical report No.4, November 2004(originally published in JFE GIHO No.4)
[14]. S.Ghosh, A.K.Sood, N.Kumar, Science, 299(2003) 1042
[15]. S.Sankar, A.Rai, B.Ankamwar, A.Singh, A.Ahmed, M.Sastry, Nature Materials, 3(2004)487.
[16]. http.//nanomission.gov.in/.
[17]. www.nanotechproject.org.
[18]. www.Sbptechnology.com
[19]. www.unitednanotechnologies.com