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Progress in the Growth and Characterization of Nano-Structured Bismuth Ferrite Thin Films

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ABSTRACT

In recent years, multiferroic thin films have generated an enormous amount of interest due to their potential application in memory devices, photovoltaic, spintronics, etc. Bismuth Ferrite (BFO) is one of the most extensively studied materials because it is the only material that exhibit magnetic order (T_N = 643 K) and ferroelectric order (T_c = 1103 K) above room temperature. This multiferroic has the potential applications in non-volatile memory devices, sensing devices, solar cells, spintronics. Researchers have been extensively working in this field of the perovskite to unearth the unanswered questions concerning its structure and phase diagrams and to exploit its properties for its various device applications. Obtaining a pure single-phase product has been problematic in the synthesis of BFO since its temperature range is very narrow and easy introduction of impurities. A wide range of investigations devoted to the synthesis of BFO using different techniques and parameters to determine the optimal conditions for the pure phase formation have been reviewed. The growth and characterization of BFO thin films have been reviewed.

1. Introduction

The past few years have witnessed the tremendous research in the materials that exhibits ferromagnetic order and ferroelectric ordering at the same time. Such magnetoelectric multiferroics were studied in 1960 and 1970 [1] but the renaissance of multiferroics [2-4] was fuelled when development and research continued in many areas of theory and equipment. The new types of multiferroics [5, 6] were identified through the production of single- crystalline samples of high quality (by high pressure routes). Moreover, the improved computational techniques assisted in the better understanding of the factors contributing to the coupling between ferroic orders [7, 8]. Lastly the thin film growth techniques helped in the synthesis of materials and phases that was not possible with traditional techniques. It also allowed the properties to be modified by the use of strain engineering [9]. Therefore the presence of high quality thin films sample together with the availability of a range of analytical tools has helped us in characterizing the multiferroic behavior more accurately. This has opened the door for us to design some multifunctional devices for future applications. Thin films multiferroics are fascinating due to its unique behavior that stimulates the exploration of more heterostructures devices.

Bismuth ferrite, $BiFeO_3$, sometimes abbreviated "BFO", is perhaps the only material that is both magnetic and strong ferroelectric at room temperature [10]. This is the reason for its popularity. The recent interest in $BiFeO_3$ were stimulated when a very high polarization and ferromagnetism was reported by Ramesh et al [11]. Other groups [12, 13] have reported that the coincidence of ferroelectric and magnetic ordering in $BiFeO_3$. This leads to an observation towards magnetoelectric coupling. It was reported by Selbach that $BiFeO_3$ is thermodynamically stable, superior to competing materials [14]. Thermal stability of lead-free piezoelectric materials has been a problem for most compositions and gives $BiFeO_3$ a strong position in this respect.

Perovskite structure Bismuth ferrite is currently the most studied multiferroic because of its large polarization and high Curie temperature. These properties make this material interesting for applications in ferroelectrics non-volatile memories and high temperature electronics. A small polarization value was observed for a bulk sample [16] as compared to the measured value of polarization for thin films that have been synthesized by variety of techniques [15, 17-20]. Initially a spread in the value of polarization can be seen [21].

The synthesis conditions of bismuth ferrite make it unusual among the bi-based perovskites because it can be made under ambient conditions as compared to others that need traditionally high pressure synthesis [22]. Further, Bismuth ferrite is popular because of the fact that it contains no lead, this making it more available for applications [23].

2. Structure of Bismuth Ferrite

$BiFeO_3$ is one of the most extensively studied multiferroic material in recent years [5, 24, 25] and the only material known to exhibit ferroelectric order (ferroelectric transition temperature T_C = 1103 K) and magnetic order (T_N= 643 K) at room temperature. $BiFeO_3$ is the only prototype among all other multiferroic oxides which shows both ferroelectricity and ferromagnetism in a single crystal above room temperature [26-28]. It has ferroelectric Curie temperature T_C = 1103 K and antiferromagnetic Neel temperature T_N = 643K [29-31]. The Bi^{3+} and Fe^{3+} ions are the ions responsible for the production of ferroelectricity and magnetism. Ferroelectricity is produced due to Bi^{3+} and antiferromagnetism is due to Fe^{3+} ions [29-31]. The properties of the material are discussed in this section.

BFO exhibits rhombohedrally distorted structure with space group symmetry R3c at room temperature. The corner positions are occupied by Bi ions, at the center of the cube (body centred position) lies the transition Fe ion and the face centers are occupied by the oxygen ions. The lattice parameters of the rhombohedral unit cell are a = 5.59 Å and α = 60.68°. In such a distorted structure, the development of spontaneous polarization (Ps) is permitted by the R_3c symmetry. The Fe-O-Fe angle controls the magnetic exchange and orbital overlap between Fe and O that determines the magnetic ordering temperature and the conductivity.

BFO unit cell expands with decreasing particle size. This is the feature shared, both with its family of ferroelectric nanoparticles, and also with all oxide nanoparticles. This is due to the surface layer relaxation and the other reason being the change of the valence of ionicity of cations among others [32].

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BFO is linear compound prepared from equal parts of Bi_2O_3 and Fe_2O_3. Different secondary phase such as $Bi_2Fe_4O_9$ (mullite phase), $Bi_{24}Fe_2O_{39}$, $Bi_{36}Fe_2O_{57}$, $Bi_{46}Fe_2O_{72}$ (sillenite type phase) and parasite ferromagnetic phase Fe_2O_3 can appear by any deviation in stoichiometry of BFO. This is owed to the highly volatile nature of Bi at high temperature and valence fluctuation in Fe ions from Fe^{2+} to Fe^{3+}. Practically it is difficult to generate pure BFO as most studies have failed to synthesize the single phase BFO samples without generating secondary phases into structure. Secondary phases can also be generated by the presence of impurities in the source material itself.

3. Basic Characterization Techniques

3.1 X-ray Diffraction (XRD)

X-ray diffraction is a powerful tool for materials characterization as well as for structure analysis. Determination of the crystal structure is an important part of the structural and chemical characterization of materials as the physical properties of solid (magnetic, electrical, optical etc.) depend on atomic arrangements of materials. X-ray patterns are used to establish the atomic arrangements of the materials because the lattice parameter, d (spacing between different planes) is of the order of x-ray wavelength. Further, it can be used to distinguish crystalline materials from monocrystalline (amorphous) materials. XRD pattern analysis helps in the structure identification and done by comparing it with the (JCPDS) which is an internationally recognized database containing the reference pattern. The following information can be obtained:

1. To judge formation of a particular material system.
2. Lattice parameters, Unit cell structure and miller indices.
3. Types of phases that is present in the material
4. Crystalline/amorphous content in the sample can be estimated.
5. Evaluation of the average crystalline size using the width of the peak in a particular phase pattern using Scherrer equation: $D = 0.9\,\lambda/\beta\cos\theta$, where λ is wave length of X-ray, β is FWHM in radian, θ is peak angle.
6. An analysis of structural distortion arising as a result of d-spacing variation that is caused by the strain, thermal distortion.

3.2 Scanning Electron Microscope (SEM)

Sample surface image is provided by SEM since it is a type of electron microscope. The image is formed by scanning the surface with a high-energy beam of electrons. The scan so performed is raster scan. For inspection of topography of the specimen at a high magnification more than 300,000X SEM is used. In SEM, the electrons interact with the atoms on the sample surface that produces signals. These signals contain the information about the topography of the surface. These signals results from the interaction between atoms at or near surface with the electrons. Signals that can be obtained from SEM include characteristic X-rays, back scattered electrons (BSE), secondary electrons, light (cathode luminescence), specimen current and transmitted electrons.

3.3 Atomic Force Microscope (AFM)

The atomic force microscope is used to obtain a 3D image of the sample. It forms an important tool for studying the top surface of thin films with the resolution at nano-scale. It measures the force between a tip and the sample. The tip is usually attached to the free end of the cantilever and is brought close to the surface of the sample. The interactions between the tip and the sample may result in attractive and repulsive forces which causes a positive or negative bending of the cantilever. This bending can be detected using a laser which can be reflected from back side of the cantilever. AFM can be operated in three modes which are contact mode, non- contact mode and tapping mode.

4. Thin Film Growth

Deposition of individual atoms is done on single crystal substrate to fabricate thin films. Although the thin film technology is a known and well-established material technology, the demand for the development of new nanomaterials is still evolving and developing. Several techniques are available for the deposition of thin films such as chemical deposition, thermal evaporation and evaporation of source materials by irradiation of energetic species. The growth process of thin films by any deposition techniques starts with a random nucleation process followed by growth stage. The deposition conditions such as growth rate, temperature, chemistry of material and substrate along with their structure affect the nucleation and growth stage. Nucleation stage can be modified by external agencies such as electron bombardment. Deposition conditions determine the crystal phase, film stress, film orientation, microstructure and associated defect structure.

Three major steps that constitute a typical thin-film deposition process are,

1. Production of the appropriate species, being it atomic, molecular, or ionic,
2. Transport of these species to the substrate through a medium, and
3. Condensation on the substrate to form a solid deposit either directly or through chemical and/or electrochemical reaction.

The unit species, on impacting the substrate are physically adsorbed on the substrate as they lose their velocity component normal to the substrate. Bigger clusters are formed as these adsorbed species interact among themselves when they move over the substrate surface as these adsorbed species are not in thermal equilibrium with the substrate. Depending on the deposition parameters, the clusters or the nuclei tend to desorb in time as they are thermodynamically unstable. If this cluster collides with adsorbed species before desorption, it grows in size. Cluster becomes thermodynamically stable on reaching a certain size limit and overcomes the nucleation barrier. The step involving the formation of stable, chemisorbed, critical sized nuclei is nucleation stage.

The critical nuclei grow in size as well as in number until a saturation nucleation density is reached. A number of parameters such as the energy of the impinging species, the rate of impingement, thermal diffusion, the activation energies of adsorption, desorption and the topography, temperature, chemical nature of the substrate are involved for the nucleation density and the average nucleus size. Growth of nucleus can be both parallel to the substrate by surface diffusion of the adsorbed species and direct impingement of the incident species leads to perpendicular growth. In general, however, at this stage the rate of lateral growth is much higher than the perpendicular growth. The grown nuclei are termed as islands.

The next stage in the process of film formation is the coalescence stage, in an attempt to reduce the substrate surface area, the small islands start coalescing with each other. The agglomeration is termed tendency to form bigger islands which is improved by increasing the surface mobility of the adsorbed species, for instance, on increasing the temperature of the substrate. In some cases, formation of new nuclei may take place on areas freshly exposed as a result of coalescence. Larger islands grow together, leaving channels and holes of uncovered substrate. At this stage, a change in the structure of the films from discontinuous island type to porous network type occurs. The formation of a completely continuous film results from the filling of the channels and holes.

4.1 Advances in the Growth of BFO Thin Films

The development of new growth and characterization techniques has evolved that led to the modern study of complex oxide materials. It offers unprecedented access to the new phases of the material. The production of non-equilibrium phases and modification of properties by strain engineering has been possible through the discovery of new thin films growth techniques [9]. For more additional information on thin films can be referred [33, 34].

The synthesis of ferroelectric, magnetic and multiferroic thin films and nanostructures have been made possible through a variety of growth techniques including sputtering, spin coating, pulsed laser deposition, sol-gel, MOCVD, many more. Generally, solid state reactions make it difficult to produce bulk BFO without impurities such as $Bi_2F_4eO_9$, $Bi_{25}FeO_{40}$. Therefore nitric acid leaching is necessary to eliminate impurity phases.

To overcome these issues, several wet chemical routes have been applied to produce pure BFO powders or films such as co-precipitation [35], microemulsion [36], sol-gel method [37-40], hydrothermal synthesis [41, 42]. Sol-gel methods have been successful in producing pure phase BFO via different routes such as citric acid route [37], ethylene glycol route [39, 43], glycol route [40] and many more [38, 44]. The sol-gel process is a widely used wet-chemical synthesis route within the fields of ceramic engineering and material science [45-47].

Many researchers, scientists and various groups are actively involved in the study and synthesis of $BiFeO_3$ thin films via different techniques e.g. (radio frequency sputtering, chemical vapor deposition, pulse laser deposition method, etc.). In comparison to the above said methods, synthesis using sol gel processing has many advantages like easy setup, cheaper, flexible control of the phase constituents and dopants, large area coverage etc. The current review summarizes some important work carried out on $BiFeO_3$ thin films by different techniques.

In a study, Huang et al [48] reported the deposition of BFO films on Si substrate and studied the effect of doping on the optical properties of the thin films. It was observed that the dopant led to a larger grain structure but less denser film and also had a potential role in improving the optical properties of the BFO films. XRD results showed that the formation of secondary and impure phases was suppressed by the dopant. The surface of BFO films was found to be uniform and dense with small size grains with clear grain boundary by AFM analysis. It was observed that the doping influenced the microstructure and morphology of the surface of the films. The maximum absorption coefficient of BLFO thin film reached an order of magnitude 105 cm^{-1} and the obtained BLFO film seemed to be promising material for photovoltaic devices. A. Z. Simões et al [50] reported that the BFO thin films were prepared using sol gel process and deposited them on $Pt/Ti/SiO_2/Si$ substrates by spin coating technique. The annealing atmosphere (air, N_2 and O_2) effect on the structure and electrical properties of the films was reported. X-ray diffraction analysis revealed that the film annealed in air is a single-phase perovskite structure and showed better crystalline nature. The presence of a single BFO phase led to lower leakage current density. Superior ferroelectric hysteresis loops at room temperature as compared to other annealing atmosphere was also observed.

Sol-gel route was followed where Zohra et al [53] synthesized bismuth ferrite thin films by sol-gel route. Copper was used as a substrate for film deposition using spin coating technique. In addition to BFO pure phase, more stable secondary phases were also observed. Smooth surface morphology was reported from SEM analysis. The average particle size was 350 nm. Linear behaviour was observed in I-V plot and resistivity was found to be of the order of 0.1 Ωcm. Though low resistivity is unexpected from the oxides but this may be due to the mixed phases that occurred in BFO thin films. Jung et al [54] synthesized polycrystalline $BiFeO_3$ thin films on indium-tin oxide (ITO)-coated glass substrates using pulsed laser deposition (PLD). A polycrystalline perovskite phase was reported by XRD analysis with a (010) preferred orientation. ITO substrate required higher deposition temperature for the crystallization of BFO thin film as compared to the Pt substrate. Smaller grain size and less leakage current density were observed on ITO substrate.

In another work, Dash et al [56] reported the preparation of phase pure $BiFeO_3$ thin films on glass, ITO and Si (100) substrates. A chemical route using spin coating technique was followed. Sol-gel process was used to prepare the thin films using precursors as bismuth nitrate and iron nitrate. Amorphous nature of the as deposited films was revealed by X-Ray diffraction and Raman spectroscopy studies. On annealing the films at 500 °C, rhombohedral crystalline phase of $BiFeO_3$ evolved, but with the presence of impurity phases such as $Bi_2Fe_4O_9$ and $Bi_{24}Fe_2O_{39}$.A drastic reduction of the impurity phases was observed on increasing the annealing temperature to 550 °C and at 600 °C, the films were phase-pure. Micro Raman spectra showed the features consistent with the reported characteristic peaks of $BiFeO_3$ crystalline phase for films annealed at 500 °C and 550 °C. Crystallite size obtained from XRD line width analysis was within 30 to 40 nm. Atomic force microscopy (AFM) however revealed grain size of ~192 nm, indicating polycrystalline nature of the grains. Pandu et al [51] concluded that it was possible to synthesize $BiFeO_3$ at low temperature using sol-gel technique. The sample was shown to be homogenous by SEM results. Sintering temperature's effect on structural and electrical properties was studied. From XRD pattern it was observed that as sintering temperature increased crystallite size increased and strain in the crystallite decreased. With increasing temperature, the crystallite size increased and a decrease in the lattice parameter was observed. In addition, an increase in grain size was observed as sintering temperature was increased. Hence, particle size followed Gaussian distribution. The Curie temperature of pure BiFeO3 is 814 °C which was very close to the ideal value 827 °C that is found by dielectric measurement.

In addition to thin films, ceramics and powders have also been synthesized. Bhole et al [52] reported the synthesis $BiFeO_3$ ceramics by solid state method. XRD analysis concluded the rhombohedral perovskite structure. The ferroelectric measurement revealed the ferroelectric nature of $BiFeO_3$ with saturation and remnant polarizations of $Ps = 0.26 \mu C/cm^2$, $Pr = 0.11 \mu C/cm^2$ respectively. It was observed that the dielectric constant and loss increased on increasing temperature. The room temperature dielectric measurement with frequency revealed that as the frequency was increased, the dielectric constant and loss decreased for $BiFeO_3$ ceramics. Further, Lui et al [49] synthesized the micro- and sub micrometer-sized BFO powders with different morphologies by sol-gel hydrothermal method. This method used KOH mineralizer. Different morphologies were observed between BFO microcrystals that were due to the crystal growth behavior that was changed which was caused by the varying OH- concentration. It was observed that using Bi-Fe-glycerol gel as precursor; submicrometer-sized particles were obtained whereas Bi-Fe-glycerol sol as precursor resulted in microspheres and microcubes. UV-vis absorption revealed that BFO powders could be used as an effective photocatalyst under visible light. Chunlin Fu et al [55] synthesized $BiFeO_3$ nanopowders at different calcination temperatures by a sol-gel process. The effect of different temperature was studied. An exothermic peak near 480.5 °C was seen in DTA curve, a temperature i.e. close to the $BiFeO_3$ formation temperature, which was in agreement with the XRD result (450 °C). After calcined at 600 °C for 1 h, XRD spectra showed several sharp diffraction peaks in correspondence with the standard XRD of the crystalline $BiFeO_3$. When calcination temperature was increased, an enhancement in the diffraction peak intensity of the XRD spectra of $BiFeO_3$ was observed and the diffraction peaks became sharper. The transition temperature from the α phase to β phase was observed near clear endothermic peak near 825.1 °C, which was in good agreement with the reported Curie temperature. An increase in the average size of powders determined by XRD and TEM with an increase in the calcination temperature was observed. A shell-core structure was distinctly observed in powders calcined at 400 °C.

4.2 Growth Factors

A large number of variables in the growth process can be used to effect significant changes in the nature of ferroelectricity in BFO. Such control and the ability to create periodic domain structures in BFO could give rise to interesting photonic devices, new pathways for nanolithography, as well as new devices that take advantage of the multiferroic nature of BFO. It was predicted by theoretical models that one could control the ferroelectric domain structure of BFO with the help of careful control of thin film heteroepitaxial growth constraints [57]. For instance it has been shown that the selection of the appropriate substrate material could result in 1D periodic ferroelectric domain structures in BFO films [58].

Focusing on heterostructures, the authors took advantage of the close lattice matching between BFO, SRO and $DyScO_3$ (DSO) (110) and the anisotropic in-plane lattice parameters of DSO. Recently, Sharma et al [59] reported a multilayered heterostructure with five alternating layers of single phase BFO and BTO thin films that were deposited using PLD technique. A remarkable increase in photocurrent and improved ferroelectric properties were observed. The two factors that resulted in good ferroelectric photovoltaic response were the low optical band gap (~2.6 eV) and high ferroelectric polarization (~60 $\mu C/cm^2$) in BFO multilayered structure.

4.3 Doped BFO Thin Films

In the last few years, in an attempt to reduce leakage currents and alter the magnetic properties, attention has also been given for studying the doped BFO thin films (both A-site and B-site doping) [60]. It was shown that a great reduction in leakage current in BFO films was observed on doping the B-site of BFO with Cr [61]. There are many studies focusing on doping BFO, but little significant impact on the physical properties has been achieved. Cheng et al [62] reported that the Nb doping helped in the improvement of the ferroelectric properties of $BiFeO_3$ thin film which controlled the leakage current. A very large remnant electrical polarization value of 80 $\mu C/cm^2$ was observed in $Bi_{0.8}La_{0.2}Nb_{0.01}Fe_{0.99}O_3$ thin film on $Pt/Ti/SiO_2/Si$ substrate. It was observed that there was a reduction in the oxygen vacancies in BFO by doping. Doping with neodymium (Nd) [64], strontium (Sr) [65], manganese (Mn) [65, 66] and lanthanum (La) [63, 67-69] have been studied with different concentrations producing different, and often conflicting results.

4.4 Strain Effect

To introduce epitaxial strain in the thin film material, thin film growth provides the ability to vary the lattice mismatch between the film and the substrate. In conventional ferroelectrics, strain effects can lead to a substantial increase of spontaneous polarization and Curie temperature [71] because the mechanism for ferroelectricity in multiferroic materials differs from that of conventional perovskite ferroelectrics. It is unclear whether the similar strain effects should be expected in thin film multiferroics.

The first principle density function calculations for multiferroics bismuth ferrite showed [70, 72] that the strain dependence of ferroelectric polarization in BFO is weak as compared with conventional ferroelectric materials and that is due to the high stability of ferroelectric state in BFO. But weak strain dependence should be expected in Bi based materials where high Curie temperature and large polarization are caused by the lone pairs of bismuth.

A finite crystallite size was observed as the synthesis of perovskites like $BiFeO_3$ turned from thin film, where the influence of epitaxial strain on the observed properties is observed, towards a wet chemical synthesis with nanoparticles as a product [73-76]. One effect of this was the relative displacement of the cations, a crystallographic measure of polarization, showing a significant value at reduced sizes, causing the antiferromagnetic order temperature TN to drop. This is promising concerning the possibility of making small nanostructures with sufficient polarization for technological applications [73].

It has been observed that much of the available literature shows that a more phase pure powder is obtained by the wet chemical synthesis of $BiFeO_3$ than that of the solid state synthesis [77, 78]. Also the latter synthesis tends to contain minor secondary phases that are clearly detected by XRD. The low intrinsic solid solubility caused this synthesis deviation from normal 1:1 stoichiometric ratio of Bi:Fe. Therefore, the nominal stoichiometry must be carefully controlled.

However, numerous authors reported these unwanted phases more or less, both in undoped and doped $BiFeO_3$ appearing in wet chemical synthesis as well. Different authors attribute this to different reasons. This could be due to the pH in which the sol is obtained or the different carboxylic acid as which carboxylic acid was used as complexing agent. In the former, Jiang et al [79] in order to reduce the formation of mullite, an increase in the pH of the precursor solution was done by adding aqueous ammonia, although mullite formation was not removed completely. Jiang et al. used citric acid as complexing agent, which was proposed by Ghosh et al [77] to be the source of the unwanted phase. It was concluded that the impurities that were seen for citric acid and not for tartaric acid was caused by the dimeric nature of the citric $BiFeO_3$-complex that doesn't promote the formation of Bi (III)-Fe (III) heteronuclear arrangement.

4. Conclusion

Multiferroic materials witness the combination of two or more ferroic orders such as ferroelectricity, ferromagnetism and ferroelasticity. A great interest for the advances and the development of the next generations of digital electronic memory devices has been observed. As bismuth ferrite has shown to possess both magnetic and ferroelectric order at room temperature, making it both scientifically and commercially interesting. The negative impact on the environment caused by using lead in mass-produced units has led to the development of lead-free materials. Various authors have synthesized the thin films where several factors affect their growth has been reviewed in an attempt to bring the recent advances in the field of lead free BFO. Various parameters play a role in the growth of BFO thin films that were discussed. We hope we tried to capture the advance in the growth of BFO thin films in this review.

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