

Heat treatment of BFO film deposited on Si (111): Spectroscopic study

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Abstract: We report the heat treatment of BFO thin film deposited on Si (111) substrate by Pulse laser deposition technique. X-ray photoelectron spectroscopy (XPS) study reveals the electronic bonds structure and stoichiometry of Bi and FeO₃. It is observed in XPS spectra that above 600 °C, Bi evaporate drastically compare to Fe and O. The quantification of Bi, Fe and O has been determined by XPS peak fitting programme. Raman spectra shows the presence of several A and E modes but the mode are diminishes at higher annealing temperature. The different modes are prominent and pronounced at 200 °C to 350 °C. X-ray diffraction (XRD) pattern shows that film deposited on Si (111) substrate does not have any single phase of BFO (BiFeO₃) rather it has tendency of amorphous structure.

I. Introduction

Work on multiferroic materials is an extensive field of research. A very good quality room temperature multiferroic property (ferroelectric and ferromagnetic) of multiferroic materials can have four states ($\pm P$, $\pm M$) semiconductor memory devices. Though individual existence of ferroelectricity and ferromagnetism are well known phenomena of some materials, but existence of both the properties simultaneously in the same material is likely to change the world of memory devices, which will be so fast that booting and shutting down time of computer will be faster than present systems. The ferroelectric or magnetic materials have already created profound technological revolution especially in data storage and memory devices and have changed our daily life style. The ferroelectric materials, which possess spontaneous electric polarization that can be switched by an applied electric field, are most widely used as memory devices (non-volatile ferroelectric random access memories (FeRAMs), dynamic random access memories (DRAM)) [07]. On the other hand, ferromagnetic materials have spontaneous magnetization that can be reversed by an applied magnetic field, and mainly used in recording and storing data as magnetic random access memories (MRAMs). But the disadvantage of ferroelectric memory is that its 'destructive read and reset operation' that limits the speed of the devices made of ferroelectric materials. But in the case of MRAMs, which can read non-destructively, but being hard ferromagnet, it possesses high coercivity. So MRAM requires high magnetic field to switch one state to another state and thus consumes high energy, which could be undesirable in high density applications [08]. In recent years numerous efforts have been put in order to get best functionality by combining ferroelectric write and magnetic read, that would enhance writing speed and reduce power consumption. This is possible in the materials which exhibit more than one functionality, known as "**Multiferroics**", which appears to overcome performance disabilities of FeRAMs and MRAMs[09]. In this perspective, last decade had witnessed tremendous interest towards multiferroic materials, not only because they exhibit ferroelectric and magnetic properties simultaneously, but also due to the cross coupling between two order parameters, termed as "magnetoelectric effect", by which an induced electrical polarization can be controlled by applying magnetic field and magnetization can be controlled by applying an electric field. This coupling effect allows one to design novel devices such as multi-state memories in which data are written electrically and read magnetically[10].

As per H. Schmid, a single phase multiferroic material is one that possesses any two of the three ferroics orders i.e. ferroelectricity (FE), ferromagnetism (FM) and ferroelasticity (FEL) [11]. But, in current research and literature the term multiferroic predominantly refers to coexistence of ferroelectricity (FE) and any type of magnetic ordering viz. ferromagnetism (FM), anti-ferromagnetism (AFM), ferrimagnetism (FRI).

In the year 2000, renaissance in the field of multiferroics was initiated by the theoretical investigation by N. A. Hill in the article, "Why multiferroics are so rare" [12]. Nicola discussed about the conditions required for ferroelectricity (FE) and ferromagnetism (FM) and showed that how the requirements are rarely met in oxide compounds. Ferroelectricity generally needs cation off centering that in turn is favoured in d^0 ions in insulators, where as Magnetic ordering needs finite electrons in d orbital often found in metals. d^0 ness and d^n ness do not exist in a single phase materials.

In this paper we report the behaviour of non-single phase BFO film with annealing temperature.

II. Experimental Details

Bismuth ferrite target was prepared by grinding the mixer of Fe_2O_3 (99.99%) and Bi_2O_3 (99.99%) for ten hours and then annealing the mixer at 850°C for one hour. The annealed sample was cooled fast and thus 20% Bi excess target was obtained. The films were prepared using pulsed laser deposition technique (Lambda Physik COMPex 201 model). The deposition conditions are: - The energy density of the KrF Excimer laser 1.5 J/cm^2 , repetition rate 10 Hz, distance between the target and substrate 5cm, temperature 750°C , Oxygen partial pressure 0.180 mbar during deposition and deposition time was 20 minutes. After deposition, temperature was held for 1h and cooling rate was $5^\circ\text{C}/\text{min}$. Raman spectra have been collected using Jobin Yvon HORIBA LABRAM HR-800 single monochromator coupled with a Peltier cooled charge couple device detector system with a overall resolution of 1 cm^{-1} .

The XRD was done using novel desktop Bruker D2 PHASER X-ray diffraction tool.

XPS spectrum was collected using SPECS Hemispherical Energy Analyzer with PHOIBOS 150-1D-DLD and remote controlled MgK α X-ray source (XR50). The X-ray power was set to 100W with emission current of 10 mA. The experiment was done in the vacuum of 1.8×10^{-9} mbar.

The sample was annealed in sample preparation chamber using e-beam annealing system [17]. The base pressure was 6.0×10^{-9} mbar and during annealing the pressure was 1.2×10^{-7} mbar. Each annealing was done for 20 min. Sample was annealed in vacuum and then it was transferred to analysing chamber from preparation chamber through vacuum using transfer rod.

III. Results And Discuss

The Raman spectrum of annealed BFO film is shown in Fig. 1. It is *in situ* annealing process and the temperature rises from 27°C to 550°C . The 13 predicted Raman active modes for rhombohedral structure using irreducible representation $T_{\text{Raman}} = 4A_1 + 9E$, comprising of four A_1 at 135, 167, 218 and 430 cm^{-1} and nine E modes at 71, 98, 255, 283, 321, 351, 467, 526, 598 cm^{-1} in polycrystalline BiFeO_3 samples [14, 15].

We observed $3A_1$ and $6E$ modes in the frequency range $100\text{--}700\text{ cm}^{-1}$. The three A_1 modes were observed at 139.31, 170.31, 216.41 cm^{-1} whereas E modes were observed at 60.85, 71.72, 74.95, 83.81, 92.23, 107.94 cm^{-1} . The peaks are shifted with higher annealing temperature and at the same time peaks are flattened with lower intensity. The peak position is shifted due to the evaporation of oxygen from the surface as well as from bulk. At higher temperature the defect created in the interstitial region of the film and due to this fact the internal strain energy is different within the sample.

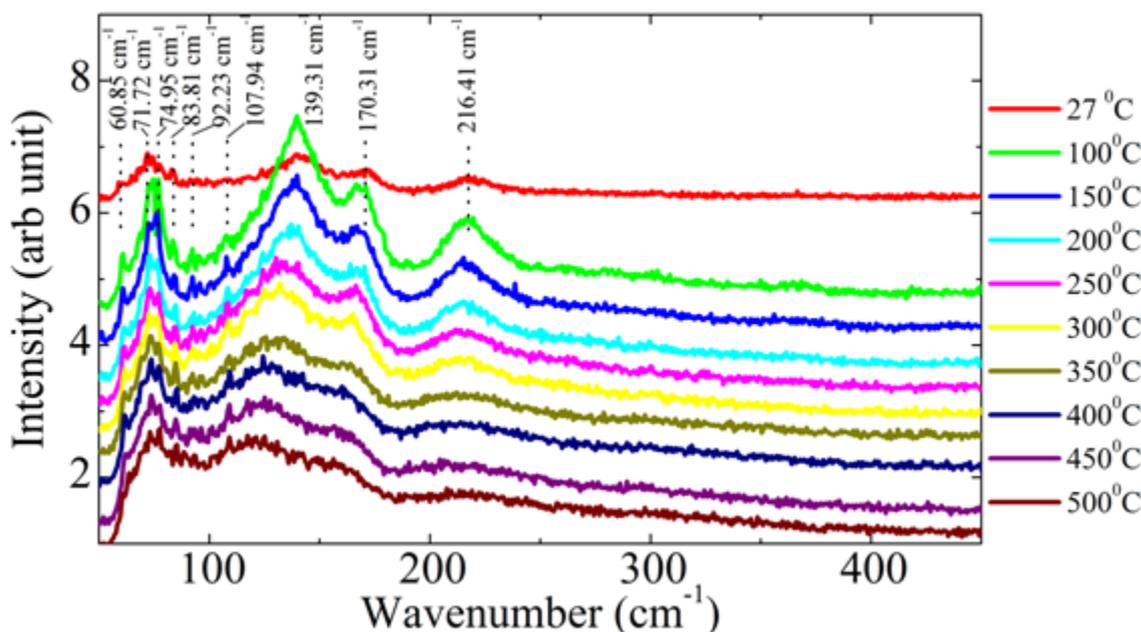


Figure 1. A typical Raman spectrum of BFO sample indicating various Raman active modes.

Figure 2, shows the full scale spectra of the deposited BFO film. It shows several Bi and Fe core peaks that indicate film is not composed of single phase. The typical XPS core level spectra are shown in Fig. 3a-i. The spectra of Bi 4f, Fe 2p and O 1s peaks were fitted using software XPS PEAK 4.1 and the binding energies were calibrated after correction of charging effects using C 1s peak at 284.5 eV .

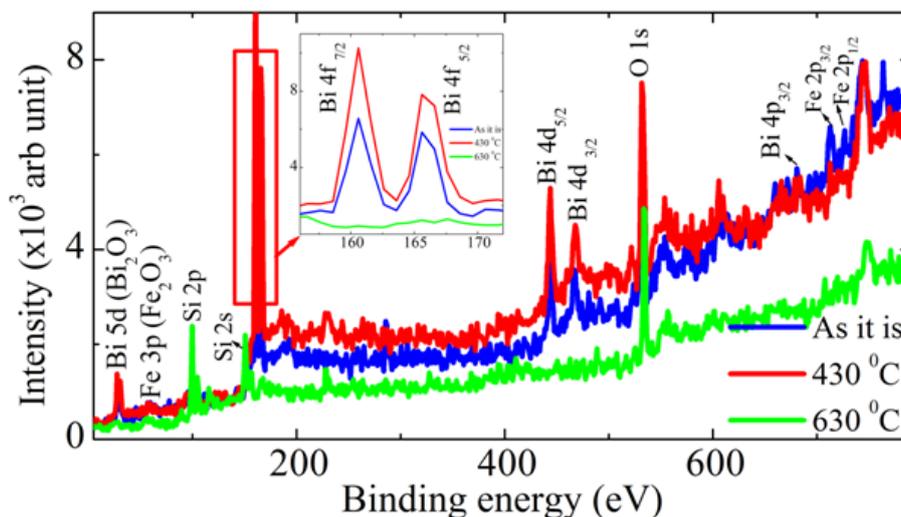
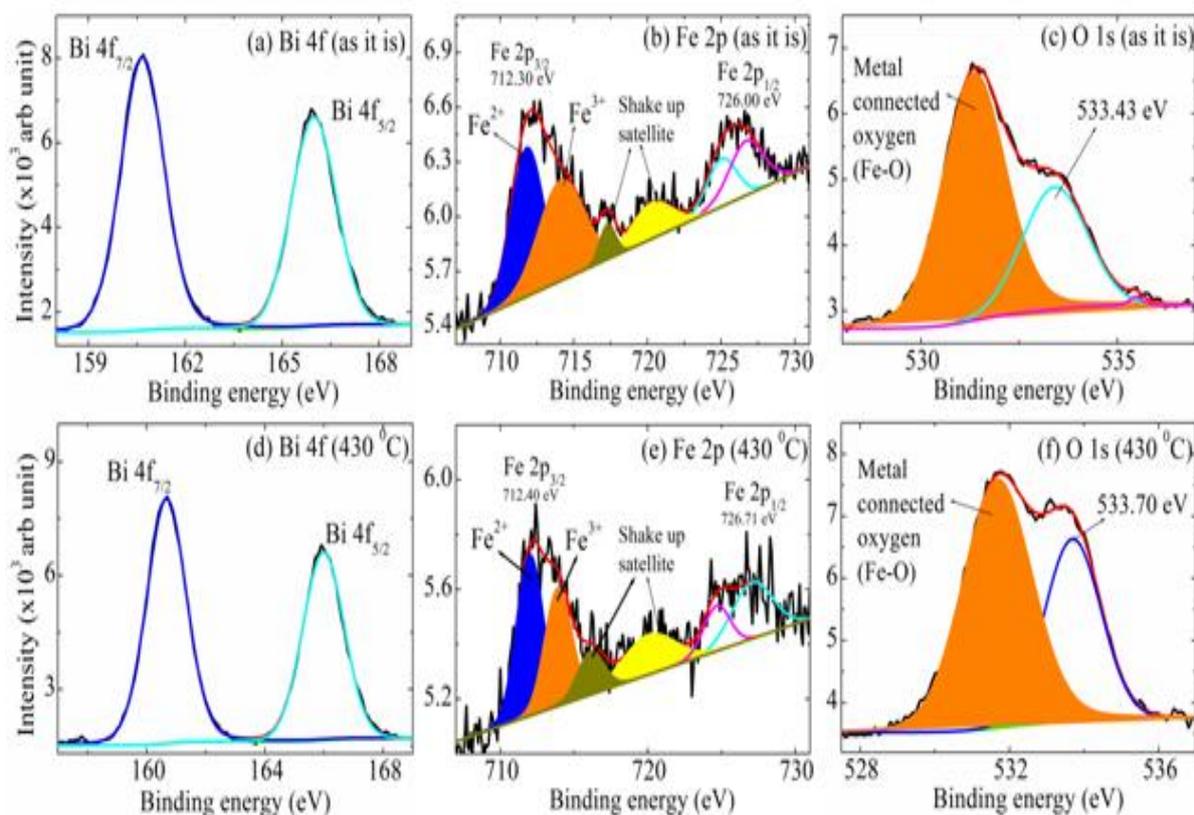


Figure 2. Typical full scale XPS spectra of BFO thin film

The bismuth ion is found to have an oxidation state of +3 as the core level spectra for Bi 4f are at 160.7 and 165.94 eV for 7/2 and 5/2 spin orbit doublet components respectively with spin orbit splitting energy of 5.24 eV. Fig. 3b, e, h, shows the oxygen has higher oxidation state

Oxygen shows two different oxidation states in Fe (Fe^{3+} to Fe^{2+}) in fig 3 a, e and h. The change in the oxidation states indicates the variety of defect structure in the stoichiometry of BFO thin film. Fe^{3+} state is observed that indicate the presence of FeO_3 phase. There is no change in peak intensity of volatile Bi at 430 °C (fig. 3d) whereas at 630 °C (fig 3g), Bi evaporates drastically and Si substrate peak is come out. A shake up satellite peak is observed around 720 eV in Fe 2p peak due to different oxidation states of $\text{FeO}/\text{Fe}_2\text{O}_3$. Fe 2p peak shows two doublet ($\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$) peaks with spin-orbit splitting energy around 13.7 eV and positioned at 712.3 eV for $\text{Fe } 2p_{3/2}$ and 726.00 eV for $\text{Fe } 2p_{1/2}$ with indication of other oxidation state of Fe which is in agreement with reported data by various authors [16].



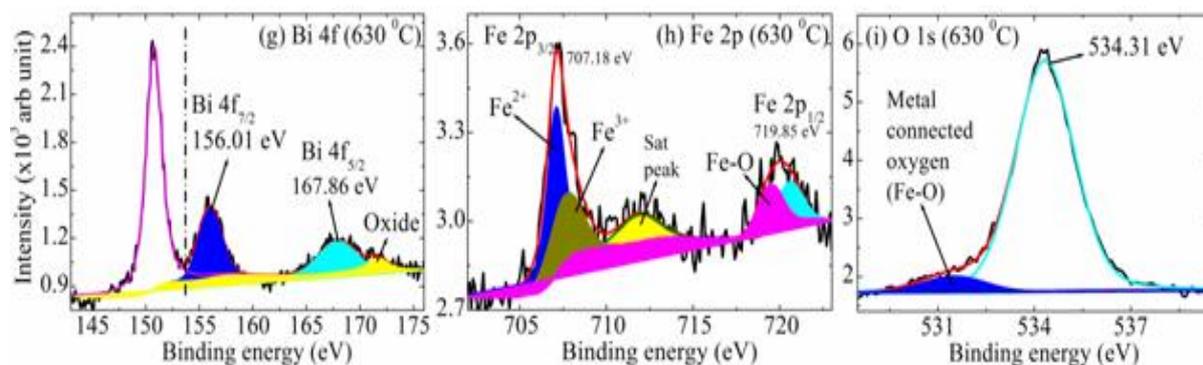


Figure 3. Typical XPS spectra of BFO thin film where as it is spectra are (a) Bi 4f, (b) Fe 2p, (c) O 1s; spectra annealed at 430 °C (d) Bi 4f, (e) Fe 2p, (f) O 1s and the spectra annealed at 630 °C are (g) Bi 4f, (h) Fe 2p, (i) O 1s.

The metal connected oxygen peak shows at near 531 eV which indicate the presence of oxygen bonding state in the deposited BFO film. At 630 °C, the percentage amount of oxygen is drastically decreases from the BFO film. The optimum oxidation values within the experimental accuracy indicate absence of iron based impurity phases, which may occur due to loss of Bi during synthesis.

The XRD patterns of the BFO thin films are shown in Figure 4. A small trace of bismuth iron oxide is observed at near 30 deg. A polycrystalline BiFeO₃ structure is observed at room temperature in XRD peak near 25 to 29 deg. Otherwise the deposited film is mostly amorphous at room temperature.

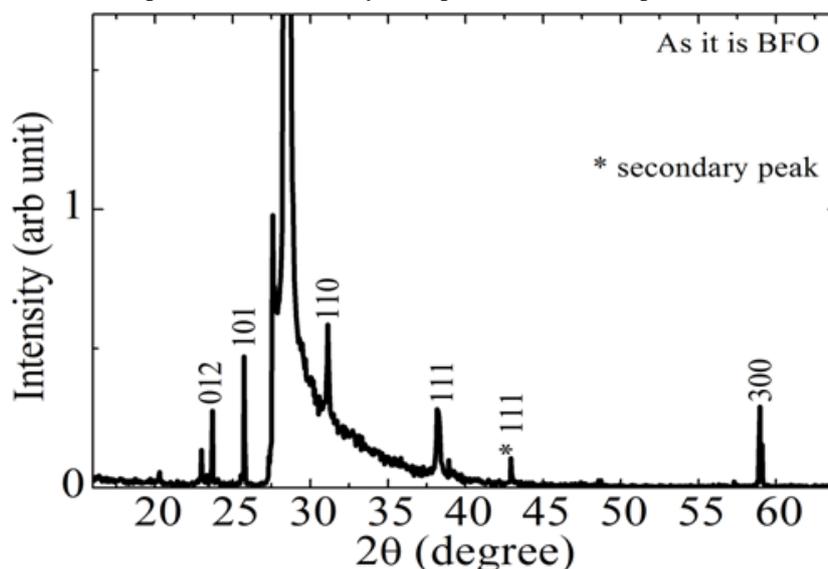


Figure 4. X-ray diffraction pattern of BiFeO₃ compound deposited on Si (111) substrate.

IV. Summary

The BFO film deposited by pulse laser is amorphous. Some conjugate bond is formed between Bi and Fe but at 630 C is broke up. In Raman spectrum the different modes of amorphous BFO film is prominent and pronounced at 200 °C to 350 °C. Three A₁ mode and 6E modes is found in Raman spectra.

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References

- [1]. M Fiebig, T Lottermoser, D Frohlic, A V Goltsev and R V Pisarev, Nature, vol. 419, pp 818, 2002
- [2]. W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature, vol. 442, pp. 759, 2006.
- [3]. M. Fiebig, J. Phys. D: Appl. Phys., vol. 38, pp R123, 2005.
- [4]. M M Kumar, V R Palkar, K Srinivas and S V Suryanarayana, Appl. Phys. Lett., vol. 76, pp 2764, 2000.
- [5]. Shreeja Pillai, Deepika Bhuwal, T. Shripathi, Vilas Shelke, J Mater Sci: Mater Electron, vol. 24, pp. 2950, 2013.

- [6]. S.M. Selbach, M. Einarsrud, T. Grande, *Chem. Mater.*, vol. 21, pp. 169, 2009.
- [7]. Kenji Uchino, *Ferroelectric Devices* 2nd Edition, CRC Press, November 4, 2009.
- [8]. Gary A. Prinz, *Science*, Vol. 282, no. 5394, pp. 1660-1663, 1998.
- [9]. J.F.Scott, "Data storage: Multiferroic memories," *Nat. Mater.*, vol. 6, pp. 256-257, March 2007.
- [10]. W. Eerenstein, N. D. Mathur & J. F. Scott, *Nature*, vol. 442, pp. 759-765. August 2006.
- [11]. H.Schmid, *Ferroelectrics*, vol. 162, no.1, pp.317-338, , 1994.
- [12]. Nicola A. Hill, *J. Phys. Chem B.*, vol. 104, pp. 6694-6709, 2000.
- [13]. A. Roy, R. Gupta and A. Garg, *Advances in Condensed Matter Phy.*, vol.2012, pp. 1-12, 2011.
- [14]. P. Pandit, S. Satapathy, P.K. Gupta, V.G. Sathe, *J. Appl. Phys.* Vol. 106, pp. 114105, 2009
- [15]. D. Kothari, V.R. Reddy, V.G. Santhe, A. Gupta, A. Banerjee, A.M. Awasthi, *J. Magn. Magn. Mater.* Vol. 320, pp. 548, 2008
- [16]. A. Lahmar, S. Habouti, C.H. Solterbeck, M. Es-Souni, B. Elouadi, *J. Appl. Phys.* 105, 014111 (2009)
- [17]. Sadhan Chandra Das, Abhijit Majumdar, Sumant Katiyal, T. Shripathi, R. Hippler, *Rev. Sci. Instrum.* 85, 025107 (2014)