Spectroscopic Study of BFO Thin Film Deposited on Si (111, 100)

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Abstract: *We report the thin film deposition of $Bi_x(FeO_3)_y$ (x and y is arbitary number) on Si (111) and Si (100) substrate by Pulse laser deposition technique. X-ray diffraction pattern shows that film deposited on Si (100) substrate do not have any single phase of BFO ($BiFeO_3$) rather it has tendency of amorphous structure. Crystallinity evolved after annealing the films at $600^\bullet C$ as the film is deposited on Si (111) substrate. X-ray photoelectron spectroscopy (XPS) study reveals the electronic bonds structure and stoichiometry of Bi and FeO_3.*

Keywords: BiFeO3, XPS, Raman, XRD

1. Introduction

Single phase bismuth ferrite, $BiFeO_3$ (BFO) is a multiferroic material and has gained importance due its stable ferroelectric and antiferromangetic coupling at room temperature, and due to the fact that it's ferroelectric properties are very much enhanced in thin film form [1-4] which can be used for the applications of very large scale integration (VLSI) in electronics industries. The synthesis of single phase $BiFeO_3$ compound is immensely difficult [5]. The constituent oxides like Bi_2O_3 and Fe_2O_3 have adverse properties as Bi_2O_3 is volatile and later one is less reactive at low temperature. It become more problematic when intermediate phases like $Bi_2Fe_4O_9$ (mullite) and $Bi_{25}FeO_{39}$ (sillenite) co-exist with zero degree of freedom according to Gibb's phase rule [6]. In this paper, $Bi_x(FeO_3)_y$ film is deposited to understand the stoichiometry and bond structure of $BiFeO_3$.

Now a days searching of multiferroic materials has become an intense field of research. If we get good quality room temperature materials which have very good multiferroic (ferroelectric and ferromagnetic) properties then we can get four states ($\pm P$, $\pm M$) semiconductor memory devices. The 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. Ferroelectric or magnetic materials have created profound technological revolution especially in data storage and memory devices, integrated circuits, that has changed our daily life style. 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)) [7]. 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).

However, the main problem with ferroelectric memory is that its 'destructive read and reset operation' that leads to the faster degradation of device, while to that MRAMs which can read non-destructively, but being hard ferromagnet, it possesses high coercivity and in order to switching magnetic states it requires high magnetic field and thus consume large energy, that could be undesirable in high density applications [8]. Efforts have been put by combining ferroelectric write and magnetic read that would enhance writing speed and reduce power consumption. Multiferroics materials appear to overcome performance disabilities of FeRAMs and MRAMs [9]. 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 spintronics devices such as multi-state memories in which data are written electrically and read magnetically [10].

The term "*Multiferroics*" had been coined by H. Schmid and by definition put by him, a single phase multiferroic material is one that possesses any two of the three ferroic oders i.e. ferroelectricity(FE),ferromagnetism(FM) and ferroelasticity(FEL) [11]. However, in current research and literature the term multiferroic predominantly refers to coexistence of ferroelctricity (FE) and any type of magnetic ordering viz. ferromagnetism (FM), anti-ferromagnetism (AFM), ferrimagnetism (FRI). In 2000, almost after four decades, a renaissance in the field of multiferroics was initiated by the theoretical investigation of N. A. Hill [12]. In this article entitled, *"Why multiferroics are so rare"* 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

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in a single phase materials. This paper created the revolution in the field of multiferroics.

Then the recent discovery of new mechanism for FE, like lone pairs in $BiFeO_3$, $BiMnO_3$ & $PbVO_3$, Geometrically frustrated magnetism in $YMnO_3$, magnetically driven ferroelectricity in $TbMnO_3$, RMn_2O_5 etc originate the revival of interest in multiferroics [13]. Among all the above one of the most promising materials is $BiFeO_3$ (BFO) because it shows room temperature ferroelectricity and anti-ferromagnetism with significant magneto-electric coupling [15]. Owing to that BFO is a prospective candidate for next generation ME memory application.

2. Experimental Details

Polycrystalline $Bi_x(FeO_3)_y$ sample was prepared by grinding the mixer of Fe_2O_3 (99.99%) and Bi_2O_3 (99.99%) for eight hours and then annealing the mixer at 850 °C for one hour. Fast cooling of the annealed sample was done. 10% Bi excess target was obtained by this process for depositing films using pulsed laser deposition technique (Lambda Physik COMPex 201 model). $BiFeO_3$ thin film is deposited on silicon substrates by pulsed laser deposition technique. 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 700°C, Oxygen partial pressure 0.011 mbar during deposition and deposition time was 15 minutes. After deposition, temperature was hold for 1h and cooling rate was 5 °C/min. Raman spectra have been collected using Jobin Yvon HORIBA LABRAM HR-800 single monochromater coupled with a Peltier cooled charge couple device detector system with a overall resolution of 1 cm^{-1}.
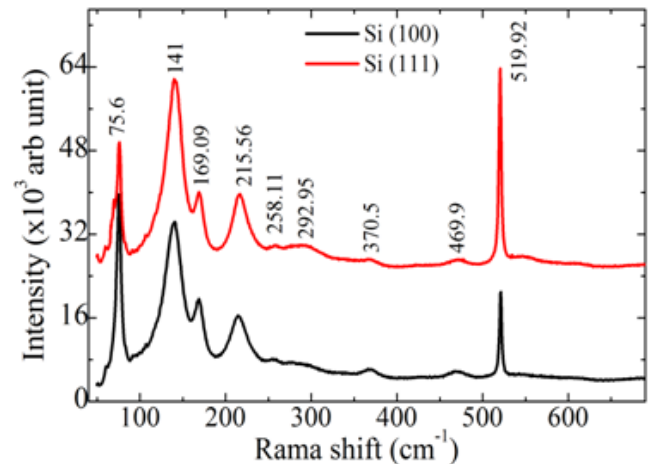
3. Results and Discuss

Figure 1: A typical Raman spectra of $Bi_x(FeO_3)_y$ sample indicating various Raman active modes.

The Raman spectra of $Bi_x(FeO_3)_y$ sample is shown in Fig. 1. Pandit et al. [14]. have reported 10 Raman active modes whereas Kothari et al. [15] observed all the 13 predicted Raman active modes comprising of four A1 at 135, 167, 218 and 430 cm^{-1} and nine E modes at 255, 283, 351, 321, 467, 526, 598, 71 and 98 cm^{-1} in polycrystalline BiFeO3 samples. We observed 4A1 and 5E modes in the frequency range 100-700 cm^{-1}. The four A1 modes were observed at 75.6, 141, 215.56 and 519 cm^{-1} whereas E modes were observed at 169.09, 258.11, 292.95, 370.5 and 469.9 cm^{-1}. The slight shift in the peak positions may be attributed to the sample preparation conditions as the peak positions of Raman vibration modes are dependent on oxygen stoichiometry and internal strain within the sample.
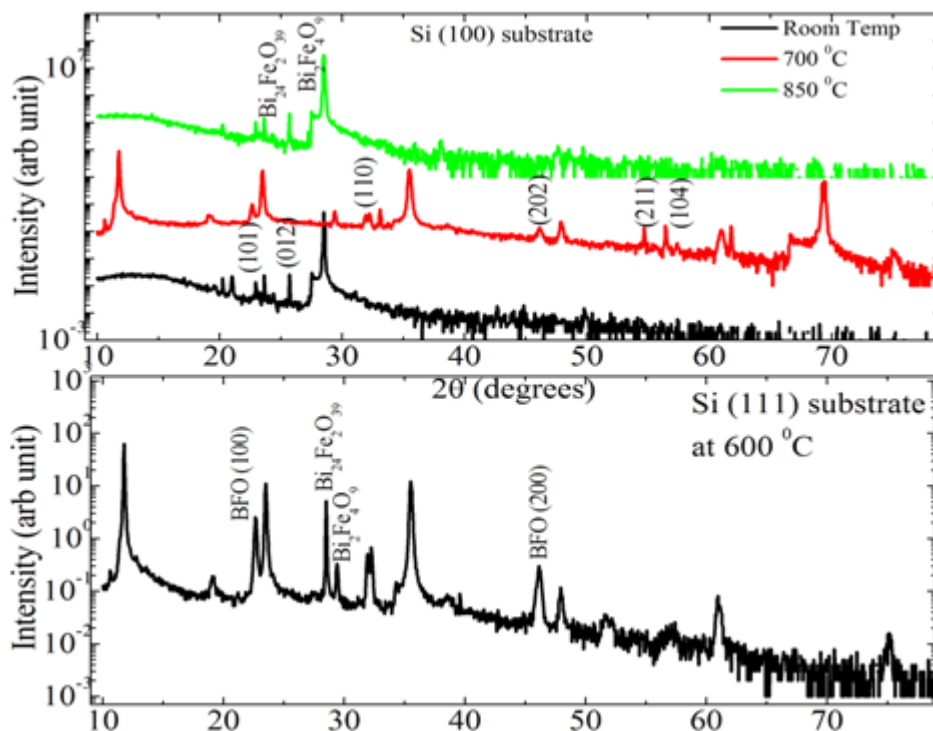

Figure 2: X-ray diffraction pattern of $Bi_x(FeO_3)_y$ compound deposited on Si (100) (up) and Si (111) (down) substrate.

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The XRD patterns of the BFO thin films are shown in Figure 2. A small trace of bismuth iron oxide is observed at near 30 deg. A polycrystalline $BiFeO_3$ structure is observed at 700 ^0C in XRD peak near 25 to 29 deg. Otherwise the deposited film is mostly amorphous at room temperature. Crystallinity evolved after annealing the films at 600°C as the film is deposited on Si (111) substrate.

The typical XPS core level spectra are shown in Fig. 4a–f. 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 C1s peak at 284.5 eV. The bismuth ion is found to have an oxidation state of +3 as the core level spectra for Bi4f are at 160.3 and 165 eV for 7/2 and 5/2 spin orbit doublet components respectively with spin orbit splitting energy of 5.36 eV. Fig. 4b shows fitted Fe 2p peak of deposited bismuth film. Fe^{3+} state is observed that indicate the presence of FeO_3 phase.
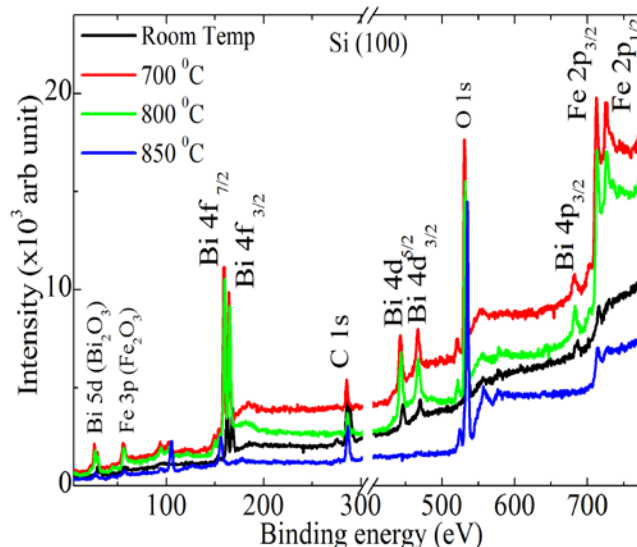

Figure 3: Typical full scale XPS spectra of $Bi_x(FeO_3)_y$ thin film

Fe 2p peak shows two wide doublet peaks with spin–orbit splitting energy of 13.2 eV and positioned at 710.3 eV for Fe 2p3/2 and 723.5 eV Fe 2p1/2 with indication of other oxidation state of Fe which is in agreement with reported data by various authors [16]. In full scale spectra shows several Bi and Fe core peaks that indicate film is not composed of single phase. The metal connected oxygen peak shows at near 529.8 eV which indicate the presence of oxygen bonding state in the deposited BFO film. At 700 ^oC, 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.
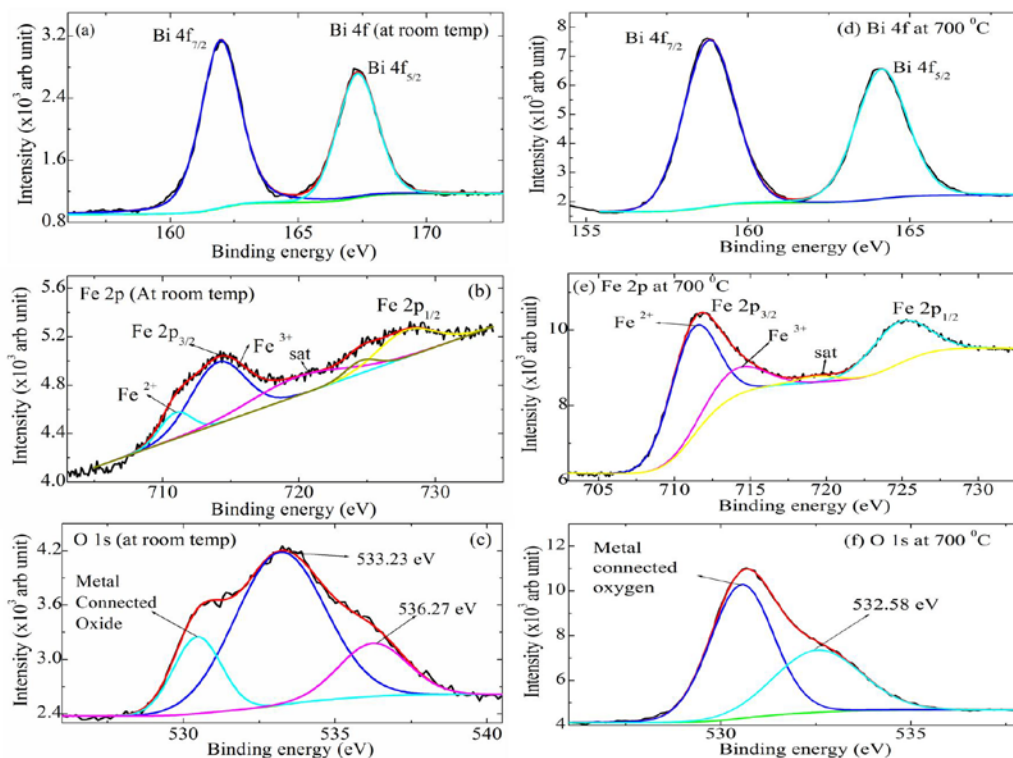

Figure 4: Typical XPS spectra of $Bi_x(FeO_3)_y$ thin film where (a) Bi 4f, (b) Fe 2p, (c) O 1s peak at room temperature whereas (d) B 4f, (e) Fe 2p and (f) O 1s peak at 700 ^oC annealing.

4. Acknowledgments

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