

Synthesis of High Resistive BiFeO₃ Thin Films for Ethanol Sensing Application Grown by PLD

Madhuri Patel¹, Cijy Mathai², Niraj Joshi^{2,3}, Ruchira Jadhav¹, Richard Pinto^{2,3}

¹Department of Electronics & Telecommunication Engineering, K. J. Somaiya College of Engineering, Mumbai

²Department of Electrical Engineering, Indian Institute of Technology Bombay, Powai

³Centre of Excellence in Nano-science & Technology,
Sahyadri College of Engineering & Management, Mangalore

Abstract: Ethanol sensors with high selectivity and sensitivity have tremendous application potential as a device in traffic management, food ferment, wine making and medical processes. Currently a large variety of metal oxide semiconductors have been tested as gas sensing materials both for ceramic and thin film gas sensors. Most of the studied gas sensors operate at nearly 200-600°C. In this paper, we report synthesis of highly resistive Bismuth ferrite (BiFeO₃ abbreviated as BFO) thin films. The BFO thin films were grown on different substrates including Si, SiO₂, platinumized silicon and quartz by using pulsed laser deposition technique. The films were deposited at different deposition conditions to obtain different grain size. The films were characterized by various techniques like XRD, AFM. The room temperature resistivity measurement on exposure of ethanol is to be carried out in order to determine ethanol sensing ability.

Keywords: BiFeO₃, Ethanol sensor, Room Temperature, Grain Size, Pulsed Laser Deposition

I. Introduction

As there is an increasing demand for various gases in industry and the home, it has become a major requirement to develop gas sensors based on the change of the resistance of a semiconductor in air caused by the presence of a reducing gas. Colorimetric indicators are commonly used for ethanol detection. The indicators are generally composed of compounds of cobalt, nickel or iron, amino acids or salen type of ligands. Manufacturing process for colorimetric ethanol sensor is patented by De Castro *et al.* in 1995 [1]. However, it has been observed that though these indicators are simple to use the sensitivity is poor and unreliable. Semiconductor gas sensors offer the potential for developing portable, rugged and inexpensive detectors. It is therefore become a major activity to develop a sensor based on the change in resistance of a semiconductor in air by alcohol vapor [2-4]. However, these sensors based on materials like SnO₂, Fe₂O₃ *etc.* though have higher sensitivity, lack in selectivity. LaFeO₃ is another material which is reported to be ethanol sensitive [5,6]. Even so, it was observed that though sensitivity and selectivity of LaFeO₃ is suitable for practical use, the shortcoming is long response and recovery time. Sol-gel derived thin films of Sr doped LaFeO₃ are shown to act as an effective ethanol sensor at 120 °C by Zao *et al.* [9]. However all the sensors, we came across function in the temperature range of 120-400 °C.

Several organic semiconductors, such as polythiophene, polypyrrole, polyaniline [10], are also been used for detecting gases, however, poor selectivity is the most serious problem for inorganic and organic conducting polymer sensing materials. To meet the need of analyzing gas mixtures, and to overcome the poor selectivity and high cost problem of popular sensors, organic-inorganic hybrid composite sensors are being intensively investigated [11]. Perovskite ABO₃ oxide materials are next promising set of materials for gas sensing as they are more stable and reliable compared to metal oxide based gas sensors. BFO is highly significant and most studied multiferroic compound material since last few years. Research has been carried out to study the gas sensing properties of BFO nanostructures of different sizes and forms. The sensitivity of BFO nanoparticle on exposure to different gases like acetone, alcohol, formaldehyde and benzene showed that the change was observed at operating temperature of 260°C [14]. Thus the above studied and developed gas sensors operate at an temperature of 240-600°C.

The preliminary study carried out by Palkar *et al.* [15] has indicated the potential of BFO thin films to sense ethanol vapors selectively at room temperature. The detection mechanism is based on the change in resistivity of the films on exposure to ethanol vapors. The change in resistivity results due to redox reaction taking place at the surface of the film. Since the reaction occurs at room temperature the sensor could be operated at room temperature unlike others. It is therefore interesting to work on the development of prototype device based on BFO thin films. BFO thin films is grown on different substrates like Si, platinumized silicon, quartz, silicon dioxide by using pulsed laser deposition technique. The films are then characterized by various techniques and sensing ability will be determined.

II. Experimental Procedure

2.1. Target Preparation

A pure polycrystalline powder was prepared by conventional solid state reaction using high purity bismuth oxide (Bi₂O₃) and iron oxide (Fe₂O₃). The powder was mixed properly and grinded for two hours. The mixed powder was then calcinated at 500^oC for 3 hours. The calcinated material was once again grinded to mix it uniformly. The material was then sintered at 800^oC for 30 min to improve the synthesis uniformity and form highly dense pallet. This target was used to deposit thin films of bismuth ferrite using pulsed laser deposition technique.

2.2. Thin film Preparation by Pulsed laser deposition

The BFO thin films were deposited on different substrates like Si, SiO₂, Pt/Si, Quartz by pulsed laser deposition technique with KrF-excimer having wavelength of 248nm under oxygen pressure in the range of 0.5-0.05mbarr, substrate temperature was varied from 600-750^oC and laser fluency was 2 J/cm². The thickness of the film was measured by Dektak profilometer. Phase analysis and growth orientation was studied by high resolution X-ray Diffractometer. The resistivity of the film was measured using four probe measurement system.

III. Results And Discussion

Fig 1 shows the XRD measurements of BFO thin films grown on PtSi. It shows that a pure perovskite structure of the film was formed and there were no any impurities or secondary phases present. It has been observed that oxygen pressure in the chamber during ablation is very critical in order to maintain oxygen stoichiometry in the films. The profilometer reading showed that the thickness of the films deposited was 200nm. The four probe resistivity measurement shows that the films are highly resistive in the range of Mega Ohms.

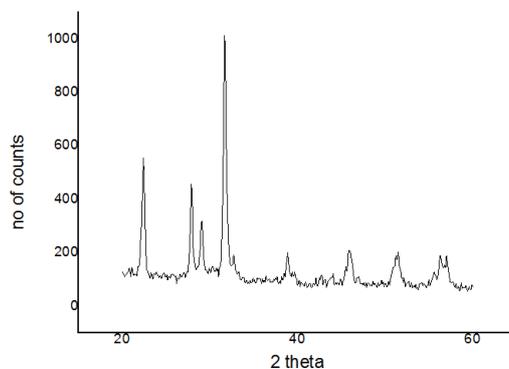


Fig 2. XRD of BFO thin film grown on PtSi.

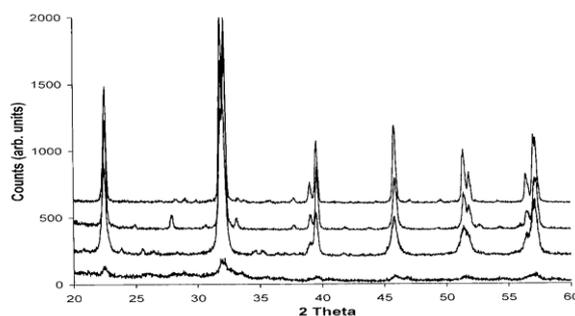


Fig 3. Comparative XRD data of BFO thin film as ref[15].

IV. Conclusion

The BFO thin films were grown on different substrates and deposition conditions so as to get the preferred oxygen stoichiometry in the films by pulsed laser deposition technique at different oxygen pressure. XRD measurement showed that the film phase is pure. The film deposited was highly resistive. To explore ethanol gas sensing properties of these BFO films, it is required to setup a measurement system which can measure high resistance in known concentration of the ethanol gas. In the following experiments we would setup the gas sensing measurement system to explore the ethanol sensing properties of BFO films.

Acknowledgement

The author is very thankful to Indian Nano electronics User Program (INUP), IIT Bombay for providing the fabrication and characterization facility to carried out the experiments at CEN, IIT Bombay under INUP, which is sponsored by Deity, MCIT and Government of India.

References

- [1]. De Castro, S. Emory, D. R. malat, US Patent application No. 758557 November 29, 1996.
- [2]. S. R. Morrison, *Sensors and Actuators* 2, 329 (1982)
- [3]. N. Yamazoe, Y. Kurakowa, T. Seiyama, *Sensors and Actuators* 4, 283 (1983)
- [4]. O. K. Varghese, L. K. Malhotra, and G. L. Sharma, *Sensors and Actuators B* 55, 161 (1999)
- [5]. J. Wu, L. Sun, J. Zhang, Y. S. Ji and B. H. Gao, *J. Transducer Tech.* 1, 1 9(1988)
- [6]. H. Obayoshi, Y. Sakurai and T. Gejo, *J. Solid State Chem.*, 17, 299 (1976)
- [7]. H. Suo, F. Wu, J. Liu, B. Xu and M. Zao, *J. Solid State Chem.*, 130, 152 (1997)
- [8]. H. Suo, F. Wu, Q. Wang, G. Liu, F. Qiu, B. Xu and M. Zhao, *Sensors and Actuators B* 45, 245 (1997)
- [9]. S. Zao, J. Kin, Xu M. Zao, Z. Peng and H. Cai, *Sensors and Actuators B* 64, 84 (2000)
- [10]. Athawale, A.A.; Bhagwat, S.V.; Katre, P.P. "Nanocomposite of Pd-polyaniline as a selective methanol sensor". *Sens. Actuators B* **2006**, 114, 263–267.
- [11]. Geng, L.N.; Zhao, Y.Q.; Huang, X.L.; Wang, S.R.; Zhang, S.M.; Wu, S.H. Characterization and gas sensitivity study of polyaniline/SnO₂ hybrid material prepared by hydrothermal route. *Sens. Actuators B* **2007**, 120, 568–572.
- [12]. 12.Q.Wan,C.L.Lin,Q.H.Li"Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors" *Applied physics letters*, 2004,vol 84
- [13]. Liwei Wang, Yanfei Kang, Xianghong Liu"ZnO nanorod gas sensor for ethanol detection", *Sensors and actuators B* 2012,162,237-243.
- [14]. Xue-Lian Yu,Yu Wang, Yong-Ming Hu,Chuan-Bao Cao, Helen Lai-Wa Chan," Gas-Sensing Properties of Perovskite BiFeO₃ Nanoparticles" *Jou.of American society*,2009,92[12],3105-3107.
- [15]. V. R. Palkar, J. John and R. Pinto Indian Patent No. 203429 (A) dated 18-12-2001.