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Integration of $BiFeO_3$ thick films onto ceramic and metal substrates by screen printing

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ABSTRACT

This study presents the preparation of bismuth ferrite ($BiFeO_3$) thick films by a screen-printing method. We explain the influence of the annealing temperature on the diffusion processes, occurring through individual layers of the thick-film structure, densification, and interface reactions between ~15-μm-thick $BiFeO_3$ films and an Al_2O_3 substrate. The key parameters were identified and include the optimal annealing temperature and substrate purity, which need to be controlled in order to obtain high quality $BiFeO_3$ thick films in terms of phase composition and microstructure. Taking into account these processing parameters, we present compositionally improved and high density $BiFeO_3$ thick films on Ag metal foil, which were sintered at temperatures as low as 740 °C. While the local ferroelectric behavior of the $BiFeO_3$ film has been confirmed by piezo-response force microscopy analysis, its macroscopic electrical response is characterized by a high electrical conductivity coupled with an interface-related diode-like current–voltage behavior.

1. Introduction

Multiferroic, lead-free $BiFeO_3$ (BFO) is a promising piezoelectric material for integration in multilayered electronic devices due to its high T_C (~830 °C [1]) and ability to exhibit both ferroelectric and antiferromagnetic ordering at room temperature [2]. The highest remanent polarization ever measured in a ferroelectric material (150 μC/cm^2) [3] was reported for BFO thin films. These properties make BFO attractive for a number of applications, such as transducers, actuators, sensors, data storage and spintronic devices [4].

The thermodynamic aspects of the BFO system [5–7], reaction kinetics between Bi_2O_3 and Fe_2O_3 [8,9], which are the commonly used starting powders for the ceramic synthesis of BFO, and sensitivity of BFO to impurities [10], make the integration of BFO onto substrates particularly challenging [11]. While BFO has been studied intensively in bulk (polycrystalline ceramics) and in thin films (thickness (t) < 1 μm), few reports have been published on the preparation and properties of BFO thick films (t > 1 μm) where the processing issues may present even greater challenges than those encountered during processing of bulk BFO ceramics. Studies on integration of BFO onto substrates as thick films are particularly important at this stage as they would provide the key step toward applications for BFO, e.g., in micro-electromechanical (MEMS) systems [12]. Especially in the case of BFO, however, the integration is demanding and not straightforward due to the readily occurring chemical reactions between the BFO layer and the electrode/substrate. In addition, differences in the coefficients of thermal expansion (CTE) of the film and the substrate can lead to stresses in the films [13–15]. Therefore, in order to prepare defect-free, high phase purity BFO thick films, both annealing conditions and the substrate material should be rigorously selected.

The first report on a BFO based thick film was by Rao and Srinivasan [16], in 1991 where a radio frequency magnetron sputtering synthesis technique was used. The composition was based on a $BiFeO_3$–$PbZrO_3$ solid solution and the resulting films were amorphous with promising magnetic properties. Since this early report, little has been reported for BFO thick films with approximately twenty publications in fifteen years, and of the publications available there is an eclectic use of substrate, composition and synthesis method. The synthesis methods reported are vast: wet chemical route [17–19], liquid-phase epitaxial growth [20], aerosol deposition [21,22], electrophoretic deposition [23], hydrothermal epitaxy methods [24], screen-printing [25], tape casting [26], and pulsed laser deposition [27]. The results of these studies, however, do not

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provide insights into the relationships between the key parameters, which are substrate, composition and synthesis method. In addition, the measured properties of the various thick films vary widely as illustrated in Table 1.

The substrate material has a critical role in determining thick film properties. Each substrate introduces its own lattice and/or thermal strain to the film and has its own adhesion properties, which may interact differently with different film compositions. With BFO-based compositions the substrate material selection is of great importance due to the high sensitivity of BFO to impurity elements and the resulting film-substrate interactions that can occur [10,28]. Chemical reactions between BFO films and substrate materials are expected, for example, Al_2O_3 stabilizes the mullite ($Bi_2Fe_4O_9$) phase, SiO_2 is known to stabilize the sillenite ($Bi_{25}FeO_{39}$) phase [10], Pt reacts with metallic Bi above 250 °C [29] and bismuth-oxide based thin films react with Pt electrodes at 800 °C forming Bi_2Pt [30].

In addition to the substrate, the synthesis methods also can have a critical impact on the film properties, such as density, adhesion, and residual stresses. It is thus not possible to establish clear relationships between the thick film properties and any of these critical parameters without a rigorous and systematic approach. Presently, no such study has been performed. It is also important to note that the data presented in Table 1 do not assist with the identification of key factors that may be used to improve the BFO-based thick film quality and properties, on a broader basis. As a result, there is a pressing need for systematic evidence of how the substrate material and synthesis method affect the BFO thick-film structure, phase composition, density and, consequently, its functional properties, such as the piezoelectric response.

Here we provide a comprehensive investigation of unmodified BFO thick films prepared by screen printing and their interactions with different substrate materials. The substrate and annealing temperatures were systematically varied and X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to provide a detailed picture of interface reactions, phase composition and film density. Those substrate-film-temperature combinations that proved to exhibit the most promising properties were also assessed for their macroscopic electrical properties, such as the current–voltage (*I–V*) behavior, and local ferroelectric properties by means of piezoresponse force microscopy (PFM) analysis. We show that the microstructure and phase composition of the BFO thick film is strongly dependent on two parameters, i.e., the impurities present in the electrode and the annealing temperature.

Table 1
Remanent polarization, coercive field and thickness of BFO based thick film structures from literature.

Structure	Film thickness (μm)	P_r (μC/cm²); E_c (kV/cm)	Reference
(0 0 1)$BiFeO_3$/$SrRuO_3$/$SrTiO_3$	2.0	20.0; 25	[24]
$BiFeO_3$/Pt/Si	5.0	7.5; 370	[21]
$BiFeO_3$/glass	10.0	0.5; 0.3	[17]
(1 1 0)$BiFeO_3$/ITO/glass	1.2	2.0; 35	[18]
$Bi_{0.95}La_{0.05}FeO_3$/$LaNiO_3$/Si	1.4	61.0; 498	[19]
$BiFe_{0.9}Co_{0.1}O_3$/Pt/ Si	1.0	59.0; 430	[27]
0.9$BiFeO_3$–0.1$Ba(Cu_{1/3}Nb_{2/3})O_3$/Pt/ Si	10.0	11.0; 154	[22]
0.67$BiFeO_3$–0.33$BaTiO_3$/YSZ	35.0	32.0; 28	[25]

2. Experimental

2.1. Powder preparation

The starting powder mixture was prepared from Bi_2O_3 (99.999%, Alfa Aesar, Ward Mill, MA, USA) and Fe_2O_3 (99.998%, Alfa Aesar, Ward Mill, MA, USA). The raw oxides were first pre-milled individually (200 rpm, 4 h in absolute EtOH) and then homogenized (200 rpm, 4 h in absolute EtOH) in a planetary mill (Retsch, PM400, Haan, Germany) in a Bi to Fe molar ratio 1:1. All milling steps were made in polyethylene vials with yttria-stabilized-zirconia (YSZ) milling balls of 3 mm in diameters. From the particle size volume distribution of the as-prepared powder mixture, measured using a laser granulometer (Microtrac S3500, Particle Size Analyzer, Montgomeryville, Pennsylvania, USA), we determined d_{50} = 0.35 μm and d_{90} = 0.84 μm.

2.2. Thick films preparation

The ink was prepared by mixing the homogenized Bi_2O_3–Fe_2O_3 powder with α-terpineol-based organic vehicle and was screen-printed onto different substrates. The BFO thick films were prepared by screen-printing three layers, each one on the top of the other one, in sequence. After each deposition step the films were dried at 150 °C for 15 min. The as-deposited and dried BFO thick films were statistically pressed at room temperature and annealed at different temperatures, i.e., at 730 °C, 750 °C, 770 °C, 800 °C, and 820 °C for 4 h with heating/cooling rates of 5 K/min.

Al_2O_3 substrates with gold electrode (herein denoted as Au/Al_2O_3) were prepared by screen-printing a commercially available Au paste (8884-G, ESL, King of Prussia, PA, USA) onto alumina substrate (99.6%, A-493 Kyocera, Neuss, Germany) with dimensions 12 mm × 12 mm × 0.6 mm. Subsequently, the Au/Al_2O_3 substrates were dried at 150 °C and annealed at 900 °C for 10 minutes with 5 K/min of a heating and cooling rate. The thickness of the gold electrode was defined to be ~20 μm. In the case of the Ag foil substrate, a commercially available, as-received, 99.9% pure metallic Ag foil was used, with 10 mm × 10 mm × 0.5 mm dimensions (Zlatarna Celje, Celje, Slovenia).

BFO thick films on Au/Al_2O_3 and Ag substrates are further denoted as BFO/Au/Al_2O_3 and BFO/Ag, respectively.

2.3. Characterization

The phase compositions of thick films were determined by XRD analysis using an X'Pert PRO MPD diffractometer with Cuα1 radiation (PANalytical, Almelo, The Netherlands). The PANalytical X'Pert HighScore software package was used to analyze the XRD patterns. This software was also used to estimate the penetration depth of X-rays in the samples during XRD analysis. The data were collected in the 2θ range from 10° to 78°, in steps of 0.017°, with an integration time of 100 s. To obtain the fractions of phases in the samples, the XRD patterns were refined using Rietveld refinement method [31] with a Topas software package (Topas version 2.1, Bruker AXS, Karlsruhe, Germany).

The density, thickness, and microstructures of the thick film samples were investigated with an SEM JSM 7600F (Jeol, Tokyo, Japan) equipped with an Inca Energy Detector (Energy-dispersive X-ray spectroscopy or EDXS). All EDXS analyses were performed at 15 keV. In addition to the surface of the as-sintered films, the cross-sections were also studied. For observations of the cross-sections, the thick films were cut with a wire saw (Precision wire saw 3242, Well, Manheim, Germany), ground with SiC papers and polished with a diamond paste (DP-Paste P 3 μm, 0.25 μm, Struers Inc., Cleveland, USA). To provide electrical conductivity of the samples' surfaces and thus prevent charging during SEM analysis, the