Surface & Coatings Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Surface anchoring of bi-functional organic linkers on piezoelectric $BiFeO_3$ films and particles: Comparison between carboxylic and phosphonic tethering groups

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ARTICLE INFO

Keywords:
Bismuth ferrite (BFO)
X-ray photoelectron spectroscopy (XPS)
Piezoresponse force microscopy (PFM)
Surface functionalization
Metalorganic chemical vapor deposition (MOCVD)

ABSTRACT

The functionalization of piezoelectric/ferroelectric bismuth ferrite ($BiFeO_3$, BFO) films and particles with bi-functional organic monolayers is reported. BFO films, grown by MOCVD adopting a bi-metallic mixed source, and BFO particles, synthetized by a sol-gel route, were functionalized either with the benzene-1,4-dicarboxylic acid (BDC) or with the phosphonobenzoic acid (PBA). The proposed functionalization route is based on an activation step of the BFO surface followed by the treatment with a BDC or PBA solution. The structural and morphological characterizations of functionalized BFO samples were carried out using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The chemical composition and the anchoring mode of the grafted monolayers were investigated by X-ray photoelectron spectroscopy (XPS) and FT-IR. Comparison of XPS and FT-IR results, obtained from BDC and PBA functionalized surfaces, gave indications on the role of the nature of the anchoring group in the functionalization process. Finally, piezoresponse force microscopy (PFM) and PFM spectroscopy studies demonstrated that the ferroelectric properties of the material are retained after the functionalization.

1. Introduction

In the last two decades multiferroics, materials in which at least two of the three ferroic orders, ferroelectricity, ferromagnetism or antiferromagnetism and ferroelasticity coexist, have attracted enormous attention [1]. In particular, the perovskite bismuth ferrite ($BiFeO_3$, BFO) is perhaps the only material to possess ferroelectric and magnetic transition temperatures well above room temperature, it has both high ferroelectric Curie temperature of about 1103 K and antiferromagnetic Néel temperature of about 643 K [2,3]. This particular behavior makes the BFO based materials, ideal candidates in applications such as data storage [4], sensors [5], spintronic devices [6], transducers [7], microwave devices [8], oscillators, phase shifters [9], heterogeneous read/write devices and so on.

In this perspective, the functionalization of BFO sounds very appealing in order to obtain multifunctional materials that combine the intrinsic multiferroic properties of the bulk with the additional properties imparted by specific coatings. Some studies report on the functionalization of the BFO surface with several polymers [10,11,12], to obtain composite materials with enhanced mechanical strength, but to the best of our knowledge no paper has reported on the functionalization of BFO surfaces with self-assembled monolayers (SAMs).

Functionalization of surfaces with SAMs has attracted considerable interest recently [13,14], since it is a versatile, accurate and low-cost method to form robust coatings imparting stability to the surface or enhancing its performances [15,16]. During the last decades, a very large number of functionalization routes have been reported to modify the surface of different metal oxide (Fe_3O_4, ZnO, TiO_2, NiO, Al_2O_3, ZrO_2, ITO) with SAMs, using various anchoring groups, among which phosphonic and carboxylic acids are the most promising linkers [17,18].

In this paper, we describe the modification of BFO surfaces (particles and films) adopting either a dicarboxylic acid, the benzene-1,4-dicarboxylic acid (BDC) or the phosphonobenzoic acid (PBA) a molecule bearing both carboxylic and phosphonic moieties, in order to compare the role of the two anchoring groups. BFO particles were synthesized by a typical sol-gel method [19], and BFO-films were grown by a Metalorganic Chemical Vapor Deposition approach (MOCVD) adopting a mixed bi-metallic source [20–22]. Among the various methods used to obtain BFO-film [23], MOCVD presents many potential advantages for deposition of BFO thin films including uniform

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https://doi.org/10.1016/j.surfcoat.2017.11.014
Received 22 June 2017; Received in revised form 15 October 2017; Accepted 4 November 2017

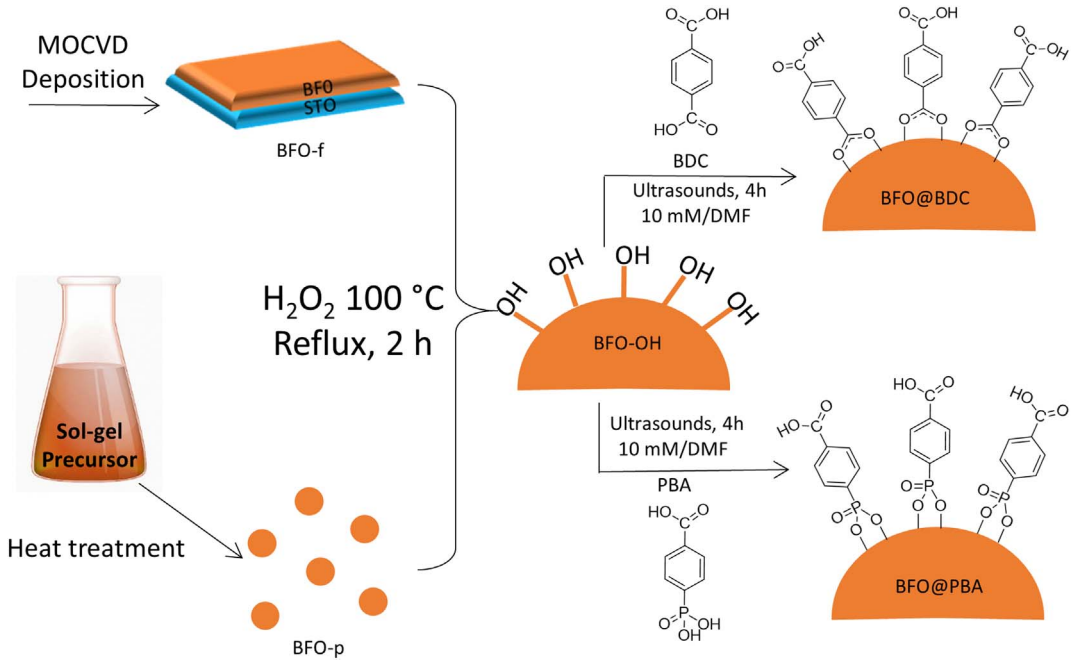

Fig. 1. Schematic illustration of the grafting process.

substrate coverage, low-cost, large scale production, control over thickness and morphology [24,21].

The surface functionalization protocol is based on a pre-activation step of both BFO films and particles with hydrogen peroxide (H_2O_2) to produce −OH groups on the surface, needed to react with the acid groups of the two chosen molecules [25].

The structural and morphological characterization of samples before and after the functionalization were studied using X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The chemical characterization of functionalized BFO surfaces was performed by X-ray photoelectron spectroscopy (XPS) for both particles and films and by FT-IR for particles. In addition the ferroelectric/piezoelectric properties of the organic functionalized BFO-films have been studied at the nanoscale level by PFM and single-point piezoresponse force spectroscopy (PFS).

2. Experimental method

2.1. Materials

Bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$, iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$, L-tartaric acid, benzene-1,4-dicarboxylic acid (BDC) were purchased from Sigma-Aldrich and 4-phosphonobenzoic acid (PBA) from Epsilon Chimie. All solvents were purchased from Sigma-Aldrich and used without further purification.

2.2. Surfaces preparation

BFO particles were synthesized via sol–gel method. $Bi(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ precursors in 1:1 ratio (5 mmol) were dissolved in 50 mL of ethylene glycol. To this, 5 mmol of tartaric acid solution was added for gelling purposes, and the solution was stirred well to obtain a homogeneous mixture. Then, the sol was heated to 80 °C to obtain a dried gel and dried to powder. Finally, the obtained as-prepared powder was annealed at 550 °C for 2 h to obtain the required BFO phase.

BFO films were deposited on $SrTiO_3$:Nb (STO:Nb) substrates at 800 °C for 1 h using a mixed bi-metallic source formed by the Bi(phenyl)$_3$ and Fe(tmhd)$_3$.The films have an orange color and are about 500 nm thick. Further details of the deposition conditions may be found in ref. 21.

2.3. Surfaces functionalization

BFO films were activated by immersion in an aqueous solution of hydrogen peroxide and then refluxed at 100 °C for 2 h, then the sample was washed with deionized water and dried under N_2. The BFO films were functionalized by immersion in the linker solution in dimethyl formamide (DMF) (10 mM) for 4 h. After grafting, the samples were removed from the solution and cleaned by rinsing in DMF. BFO particles were first sonicated for 30 min in a round bottom flask and then refluxed with an aqueous solution of hydrogen peroxide at 100 °C for 2 h. Then the particles were recovered by centrifugation and washed with deionized water and then dried. The activated particles were functionalized by dispersion (100 mg) in a linker solution in DMF (10 mM). The dispersion was stirred for 4 h, and then particles were collected by centrifugation at 6000 rpm for 10 min. After the grafting, particles were cleaned by re-dispersion in DMF and recollection by centrifugation (2 cycles).

2.4. Characterization

XPS spectra were run with a PHI 5600 multitechnique ESCA-Auger spectrometer equipped with a standard Mg K_α X-ray source. Analyses were carried out at a 45° photoelectron angle (relative to the sample surface) with an acceptance angle of ± 7°. The XPS binding energy (BE) scale was calibrated by centering C 1s peak due to hydrocarbon moieties and "adventitious" carbon at 285.0 eV [26]. Film structure was analyzed by XRD in glancing incidence mode (0.5°) using a Smartlab Rigaku diffractometer, equipped with a rotating anode of Cu K_α radiation operating at 45 kV and 200 mA.

Transmission FT-IR measurements were recorded on a JASCO FT-IR 430, using the KBr pellet technique, with 100 scans collected per spectrum (scan range 560–4000 cm^{-1}, resolution 4 cm^{-1}). FE-SEM micrographs were obtained using a ZEISS SUPRA 55VP field emission microscope. The energy dispersive X-ray analysis (EDX) spectra were recorded using an INCA-Oxford windowless detector, having a resolution of 127 eV as the FWHM of the Mn K_α.