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Chemical solution deposition and characterization of $BiFeO_3$ thin films

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Abstract

One of the most interesting category of multifunctional systems is the magnetoelectrics (ME), i.e., materials having simultaneous magnetic and ferroelectric activity.

The present paper describes a simple low-temperature synthesis method of preparing bismuth ferrite thin films by a wet chemical route, using bismuth and iron nitrates and two chelating agents (citric acid and polyvinyl alcohol). The films were layer by layer deposited on substrate (silica glass) using the dip-coating technique. The thickness of the layers were controlled by viscosity of the solutions and withdrawing speed parameters. After specific annealing, in air, the samples were characterized by scanning electron microscopy SEM, spectroelipsometry SE, X-ray photoelectron spectroscopy XPS, Raman spectroscopy.

A more thoroughly control of the processing parameters seems to be essential in obtaining $BiFeO_3$ thin films. Solution chemistry variations (differences in precursor type) can have a significant impact on the film properties.

Keywords: Films; Spectroscopy; Optical properties; $BiFeO_3$

1. Introduction

$BiFeO_3$ – BFO – is known to be the only material that exhibits multiferroism at room temperature. It is a rhombohedrally ($R3c$) distorted ferroelectric perovskite with $T_c \sim 827\,^\circ C$ (1100 K) and shows G-type antiferromagnetism up to 370 °C (643 K) $\sim T_N$.[1–3]

However, BFO shows unexpectedly small values of the ferroelectric polarization P_s even in a single crystal. Wang et al.[4,5] have fabricated an epitaxial monoclinic pseudotetragonal BFO film having a $P_s \sim 90\,\mu C/cm^2$ almost one order of magnitude higher than that of the bulk BFO by applying a strong compressive stress imposed by the bottom structure, $SrRuO_3/SrTiO_3$. It seems that the method of preparation and deposition of films plays a significant role on their properties.

One practical way to obtain thin ceramic films is the solution deposition technique. The general principle involved in the solution deposition of films is to prepare a "homogeneous" solution of the necessary cation species that may later be coated to a substrate. The fabrication of thin films by this approach involves four basic steps: (i) synthesis of the precursor solution; (ii) deposition by spin-coating or dip-coating, where drying processes usually begin depending on the solvent; (iii) low-temperature heat treatment for drying, pyrolysis of organic species (typically 300–400 °C), and formation of an amorphous film; (iv) higher temperature heat treatment for densification and crystallization of the coating into the desired oxide phase (600–1100 °C). For most solution deposition approaches, the final three steps are similar despite differences in the characteristics of the precursor solution, and for electronic devices, spin-coating has been used almost exclusively. Depending on the solution route, different deposition and thermal processing conditions may be employed to control film densification and crystallization for the preparation of materials with optimized properties.[6] Film properties that could involve changes in solution chemistry

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include poor thickness uniformity (striations), crack formation, crystallization behavior and phase purity, and compositional nonuniformities.

For the production of thin films, the most frequently used CSD approaches may be grouped into six categories: (1) sol–gel, (2) chelate processes, (3) metalloorganic decomposition (MOD) routes, (4) nitrate method, (5) citrate route and (6) Pechini process.

The citrate process has been used to fabricate a variety of multicomponent electronic ceramic materials. The citrate solution synthesis process is similar to Pechini process, except that ethylene glycol or other polyhydroxy alcohols are not utilized.

In this work we have obtained $BiFeO_3$ thin ceramic films using citrate route. In a second method we have used polyvinyl alcohol instead of citric acid.

2. Experimental

To produce citrate precursor solutions, stoichiometric amounts of the desired metal nitrates are dissolved in water and citric acid is then added to form citrate species. This process results in solution species that have a lower organic content than in Pechini process, and consequently, films that display less weight loss during conversion to the ceramic phase. In a second route we used polyvinyl alcohol instead of citric acid. As precursors $Bi(NO_3)_3\cdot5H_2O$ and $Fe(NO_3)\cdot9H_2O$ were used. The 0.1 M $Bi(NO_3)_3$ and 0.1 M $Fe(NO_3)_3$ solutions were prepared by dissolving the corresponding metal nitrate in diluted HNO_3 (HNO_3:H_2O 1:5 volume ratio). The 0.1 M citric acid (samples label C_n, n representing the number of layers) or 2.5 wt.% polyvinyl alcohol (samples label P_n) solutions were added as chelating agents. The solutions (0.1 M $Bi(NO_3)_3$:0.1 M $Fe(NO_3)_3$:chelating agent) were mixed in 1:1:1 volume ratio. From the two final solutions (C and P) the films were deposited on silica-soda-lime glasses by dipping using a withdrawal rate of 5 cm/min. Solution temperatures and viscosities were controlled. The films were thermally treated with a heating rate of 1 °C/min up to 500 °C where a 1 h plateau was maintained.

Samples with a multilayered structure were deposited in order to achieve films with desired thickness, sometimes impossible to be obtained by only one deposition. On the other hand the thickness of the film cannot be simply obtained by multiplying the thickness of one layer by the numbers of depositions, because each layer from the multilayered structure suffers a different number of thermal treatments, and more than that each new deposited film interacts with the previous one.

Spectroellipsometric (SE) measurements on the $BiFeO_3$/glass samples have been made in the 400–700 nm wavelength range at an angle of incidence of 70°. Room temperature Raman spectra were recorded in back-scattering geometry by using a Jobin Yvon/Atago-Bussan T-64000 triple spectrometer with a liquid nitrogen cooled CCD detector. Micro-Raman measurements were carried with a 90× microscope objective and the laser spot size was around 1–2 μm. The surfaces of samples were excited by 514.5 nm light with a power not exceeding 50 mV from an Ar ion laser. We measured X-ray photoelectron spectroscopy (XPS) using a Quantum-2000 (ULVACPHI) spectrometer (Al Kα X-ray source).

3. Results and discussion

Room temperature structure of $BiFeO_3$ was reported in literature as a highly distorted rhombohedral perovskite with a space group of $R3c$.[7,8] This rhombohedral geometry (R phase) gives 15 Raman-active modes: $\Gamma = 4A_1 + 9E$. Although Raman spectra of bulk BFO materials are regarded as starting point in studying thin films of BFO[7], however different dielectric properties of films and bulk materials arise to some extent unlike behavior.[9]

Fig. 1 exhibits room temperature Raman spectra of bulk $BiFeO_3$ (as obtained by us, similarly to the one reported in Ref. 7) and of two BFO films on glass substrate obtained with two different chelating agents: polyvinyl alcohol (BFO-P2) and citric acid (BFO-C2). As expected both films shows similar spectra to bulk BFO material except for some up-shifted frequency peaks and the peak located at about 92 cm^{-1} which seems to decrease drastically for both films. Singh et al.[8] assigned the four peaks at 136, 168, 215, 425 cm^{-1} to A_1(LO-TO) modes and peaks located at 275, 335, 363, 456, 549 and 597 cm^{-1} to E(TO) phonons in polarized Raman spectra on BFO films with R3c symmetry. Similarly our spectra point out the presence of $R3c$ phase. Due to the reduced intensities and widened peaks one can conclude that the two films have lowered crystallinity in comparison to the bulk $BiFeO_3$ in the following succession: $BFO_{bulk} > BFO\text{-}C2 > BFO\text{-}P2$.

Experimental SE spectra have been fitted using a new model based on multilayer and multicomponent Bruggemann's effective medium approximation (B-EMA).[10] While the already published model[11] consists in a mixture of the dielectric constants of Bi_2O_3 and Fe_2O_3, this new one included also the dielectric constants of the solution precursors. The following components have been used as references in the simulation program: Bi_2O_3, a 1:1 volumetric mixture of $Bi(NO_3)_3$:$Fe(NO_3)_3$

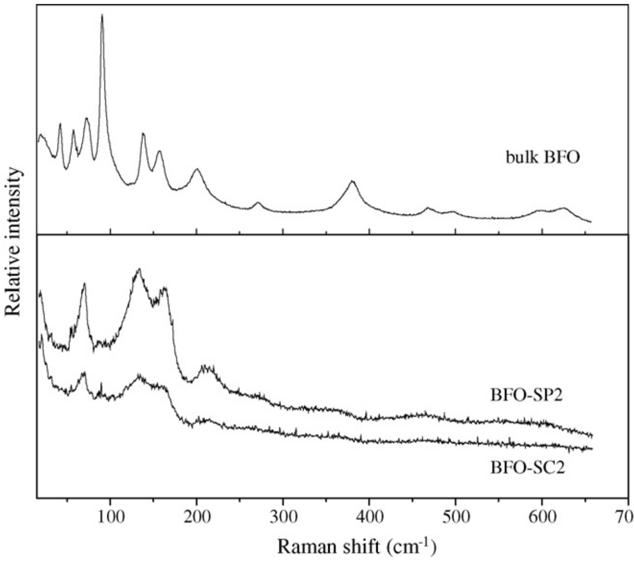

Fig. 1. Raman spectra of bulk $BiFeO_3$ and of two $BiFeO_3$ films: BFO-SP2 and BFO-SC2.

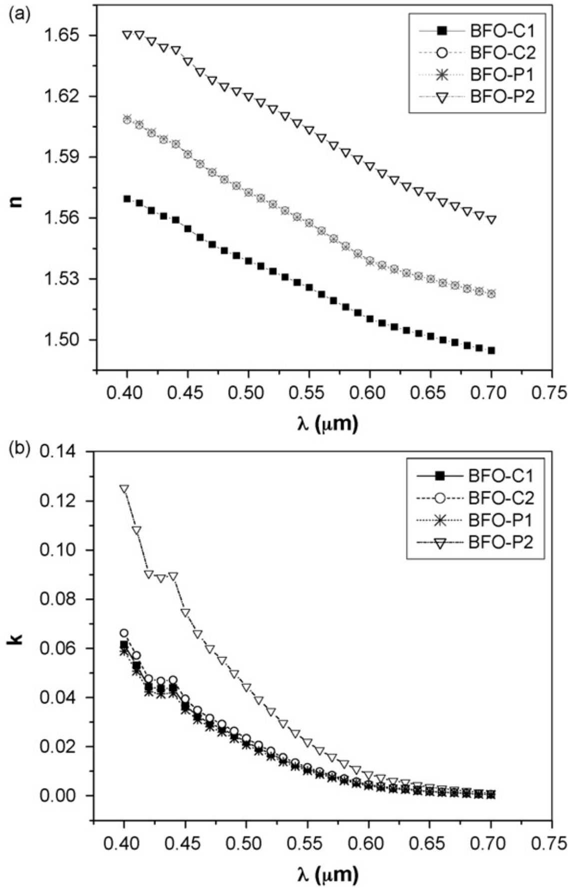

Fig. 2. The refractive index, *n*, for the C-type and P-type samples (a) and the extinction coefficient, *k*, for the C- and P-type series, respectively (b).

termed as "Bi + Fe NO_3"—see Table 1, $Bi(NO_3)_3$, Fe_2O_3, $Fe(NO_3)_3$ and voids. While the dielectric functions of Bi_2O_3 and Fe_2O_3, were taken from literature databases,[12] the "Bi + Fe NO_3", $Bi(NO_3)_3$, and $Fe(NO_3)_3$ were measured by a Pulfrich-type refractometer. The volume fractions of the components and the thickness of the layers were used as fitting parameters. The thickness of the samples (d) and the volume fractions of the components for the C and P samples with one and two layers, obtained from the best fit, are presented in Table 1, while the optical constants (n and k), for the same samples, are shown in Fig. 2(a) and (b). Both precursors induce a slightly different behaviour of the films regarding optical constants, films thickness and composition. The C-type samples leads to films with smaller n, k and d ($n = 1.558$ at $\lambda = 0.55\,\mu m$) and Δd (difference in thickness between the second and the first layer, see Table 1) in the range of 147–200 nm—confirmed also from SEM images, in comparison with the P-type samples ($n = 1.604$ at $\lambda = 0.55\,\mu m$ and $\Delta d \sim 220$–270 nm). These observations were correlated with complementary chemical and structural methods. Detailed XRD analysis has been presented in a previous paper[12] and is in accordance with the above observation.

Data obtained from XPS analysis show that Fe2p as well as Bi4f exhibit typical 3+ oxidation states (Fig. 3) with a lower concentration of Fe^{3+} on the top of the surface as a result of a possible Bi segregation to the surface. It must be emphasized the XPS sensitivity to the outermost surface layer meaning that only the first 20–30 monolayers (a few nm) can be detected. Carbon is present on the surface as the main contaminant but the detection of Si2p at 102.4 eV together with the appearance of the Na1s at 1072 eV reveal the presence of silicates from the substrate resulted from film nonuniformities and/or imperfections. Oxygen O1s (530.7 eV) is bonded mostly on Bi^{3+}.

SEM micrograph underlined the thickness of the ceramic films (Fig. 4(a) and (b)). The cracks evidenced in the micro-

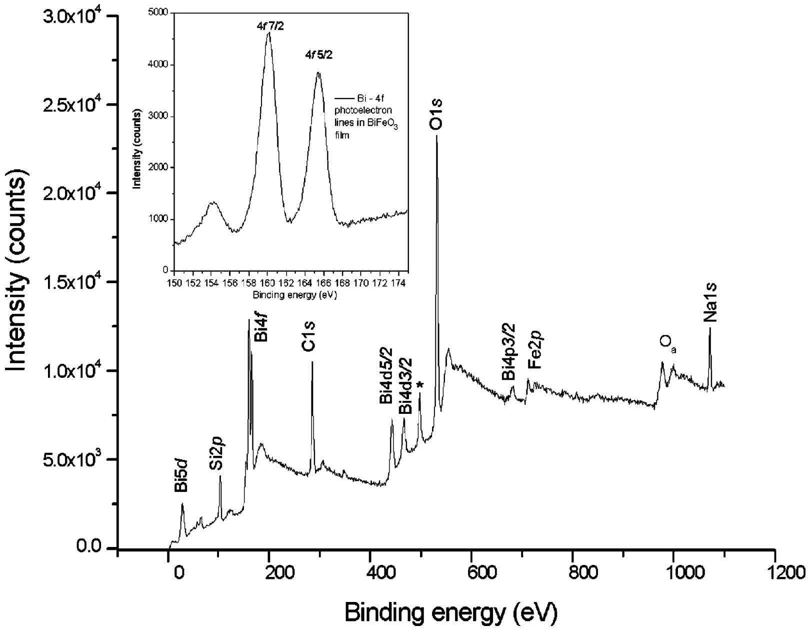

Fig. 3. XPS survey of $BiFeO_3$ two layers films onto a glass substrate annealed 1 h at 500 °C. Inset, Bi4f core-level spectrum. *Satellite line due to oxygen contaminated Al anode.

Table 1
Thickness (*d*) and volume fractions of the components of $BiFeO_3$ samples obtained from the best fit of the experimental ellipsometric data

Sample	*d* (Å)	Bi_2O_3 (%)[a]	"Bi + Fe NO_3" (%)[b]	$Bi(NO_3)_3$ (%)[b]	Fe_2O_3 (%)[a]	$Fe(NO_3)_3$ (%)[b]	Voids (%)	$\Delta d_{(lay1-lay2)}$ (nm)
BFO-C1	1800	8.29	54.78	12.51	12.26	6.16	6.00	208
BFO-C2	3680	11.95	49.24	14.09	12.62	6.30	5.80	
BFO-P1	1080	14.09	51.84	11.67	11.25	5.87	5.27	255
BFO-P2	3630	0.10	63.29	6.05	22.36	4.30	3.90	

[a] Optical databases (e.g., http://www.luxpop.com).
[b] Precursors solutions.

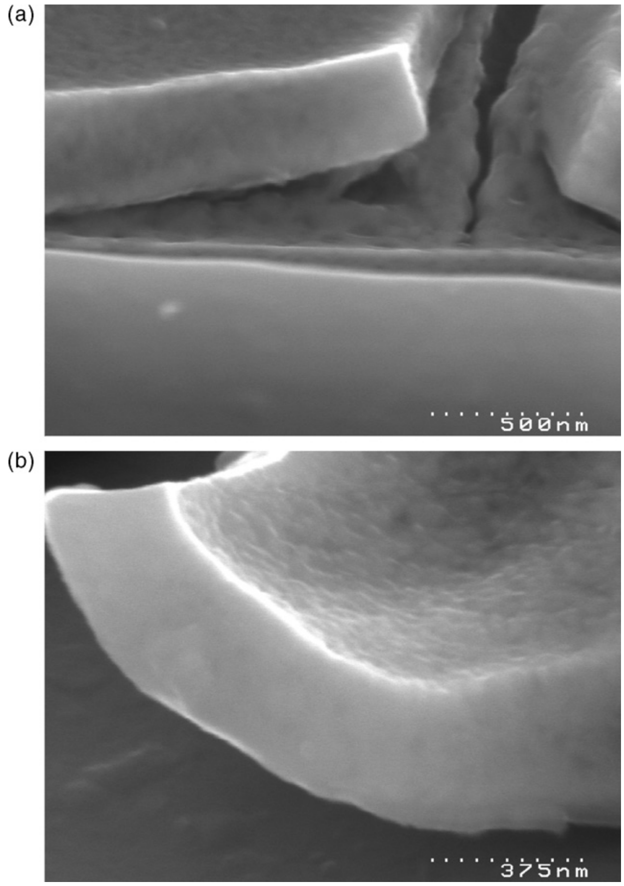

Fig. 4. SEM micrograph of the BiFeO3 thin films after two annealing treatments at 500 °C/1 h: (a) C2 sample; (b) P2 sample.

graphs were special obtained by scratching the surface to see the thickness and its transversal microstructure. SEM observations are in agreement with the SE and XPS data. Also one notices some imperfection of the films such as variation of the thickness and the existence of pores and cracks. A better control of the processing parameters seems to be essential in the case of $BiFeO_3$ thin films microstructure.

4. Conclusion

A wet chemical route, using two kinds of chelated agents – citric acid or polyvinyl alcohol – was adopted to obtain $BiFeO_3$ thin films. This method offers reproducibility of the film thickness. On the other hand, by using chelating agents the porosity (optical constants) of the films can be controlled.

After the thermal treatment the films morphology is changed with a continuously variation in the volume fractions of the components, optical constants (*n* and *k*) and thickness. Both C- (citric acid) and P-type (polyvinyl alcohol) samples become denser, as the voids content decreases, which exhibit a clear tendency of crystallization but smaller than in the case of bulk $BiFeO_3$—revealed by Raman results. In this respect, the following succession was found: $(BFO_{bulk}) > (BFO\text{-}C2) > (BFO\text{-}P2)$.

In the near surface region one may be noticed the lower relative concentration of Fe suggesting a possible Bi segregation to the surface and/or Fe diffusion into film.

Different precursors can have a significant impact on the film properties.

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