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Preparation of $BiFeO_3$ films by wet chemical method and their characterization

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Abstract

Multiferoic materials (having coupled electric, magnetic and structural order parameters that result in simultaneous ferroelectricity, ferromagnetism, and ferroelasticity) present opportunities for potential application in information storage, the emerging field of spinotronics and sensors. The perovskite $BiFeO_3$ is ferroelectric [Curie temperature (T_c) ~1103 K] and antiferromagnetic [Neél temperature (T_N) ~643 K], exhibiting weak magnetism at room temperature. Conditions for synthesizing single $BiFeO_3$ phase are critical since the temperature stability range of the phase is very narrow. Moreover, it is also difficult to control oxygen stoichiometry in the sample.

In this work the preparation of $BiFeO_3$ thin films by a specific wet chemical route is discussed. Respective influence of the precursors, thermal annealing condition, the substrate and, generally speaking, the preparation process of the films is presented.

Results obtained by X-ray diffraction and spectroscopic elipsometer (SE) was used to characterize the obtained films.

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

1. Introduction

Magnetoelectric (ME) effect, first presumed to exist by Curie,[1] also called multiferroic, exhibit both ferroelectric and magnetic ordering. Recent interest in these materials is driven by their potential application in memory devices and sensors. $BiFeO_3$ is one of the few magnetoelectric materials exhibiting ferroelectric properties in a wide range of temperature. Wang et al.[2,3] reported multiferroic behavior, with ferromagnetic and ferroelectric polarizations that are both large at room temperature, in thin strained films of $BiFeO_3$ (BFO). Although at room temperature, bulk BFO is ferroelectric and antiferromagnetic,[4–8] Wang et al.[2] reported that a 70-nm film shows both an enhanced ferroelectric polarization (90 $\mu C\,cm^{-2}$) and a substantial magnetization (1 μ_0/Fe). This remains the only report of a robust room temperature multiferroic and suggests the potential for novel devices that exploit the anticipated strain-mediated magnetoelectric coupling between the two ordered ground states. There results demonstrated a thickness dependence in these properties, and suggested that a likely explanation of these effects was that heteroepitaxial strain induced a monoclinic distortion, relaxing gradually with increasing thickness. Detailed X-ray studies have shown evidence for such a monoclinic structure, as well as no evidence for secondary phases. The out-of-plane lattice parameter for the BFO layer progressively increases as the thickness is decreased, consistent with the expected effect of epitaxial constraint. Another possibility, originally suggested by Teague et al.,[9] is that high leakage in the bulk samples, somehow reduced in the films, could have prevented prior researchers (over the past four decades) from observing the large value of spontaneous polarization of BFO. In there comment, Eerenstein et al.[10] argue that epitaxial strain does not enhance the magnetization and polarization in $BiFeO_3$. They conclude that an increased thickness dependent magnetization is not an intrinsic property of fully oxygenated and coherently strained epitaxial BFO films that exhibit a high electrical resistively. If it is only possible to achieve substantial magnetization values in deoxygenated BFO, then the applications potential is reduced, because an increased electrical conductivity will be detrimental to ferroelectric performance.

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The above mentioned controversy underlines the importance of BFO films and their potential application. So, the obtaining of thin films of good qualities becomes an important task for studies and application. In this work we tried to control the thickness of the films using a wet chemical route. The obtained films were characterized by mean of spectroscopic elipsometry.

2. Experimental

Thin films were deposed onto a glass substrate following the sol–gel aqueous route. As precursors $Bi(NO_3)_3$ $5H_2O$ and $Fe(NO_3)$ $9H_2O$ were used. The 0.1 M $Bi(NO_3)_3$ solution was prepared by dissolving 4.9 g $Bi(NO_3)_3$ $5H_2O$ into 100.0 ml (1:5 HNO_3:H_2O). Citric acid (label CB_n, n representing the number of layers) and polyvinyl alcohol (label PB_n) solutions were added as chelating agents. From these two solutions the films were deposited on silica-soda-lime glasses by dipping using a withdrawal rate of 5 cm/min. Solutions temperature, viscosity and pH were controlled. The films were thermally treated with a heating rate of 1 °C/min at 500 °C where a 1 h plateau was maintained.

The annealed films were characterized by X-ray diffraction (XRD). X-ray diffraction data were collected using a Shimadzu XRD 6000 diffractometer with Cu Kα radiation at a step of $1.2^\circ\ \mathrm{min}^{-1}$ in the range $2\theta = 10$–70°. The structural and optical characterization of $BiFeO_3$ multilayer thin films was made by the spectroscopic ellipsometry (SE). The measurements were carried out in air, in the 400–700 nm wavelength range at an angle of incidence of 70°. The acquisition interval of the data was 10 nm and the reading accuracy of azimuths was 1 min. The SE spectra were fitted using the multilayer and multicomponent Bruggemann Effective Medium Approximation[11] (BEMA). The volume fractions of the components and the thickness of the layers were taken as fitting parameters.

3. Results and discussions

After each deposition followed by annealing treatments at 500 °C the samples were characterized by mean of X-ray diffraction and spectroscopic ellipsometry. The films had good adherence and uniformed spread on the glass support. The colour become light brown as the number of layers increased. In Fig. 1 are presented the XRD profile curves characteristic of 4 layers depositions of citric acid precursor solutions (CB) and polyvinyl alcohol (PB) precursor, respectively. One can notice some differences between the two samples; CB based solution present more crystallised peacks than PB based solution inferring that citric acid effect as chelate agent is more efficient. That may be explained by the presence of the active group –COO⁻. Characteristics peaks of $Bi_2Fe_4O_9$, as secondary phase, were observed for polyvinyl alcohol based precursor solution, suggesting that annealing treatment at higher temperature are necessary.

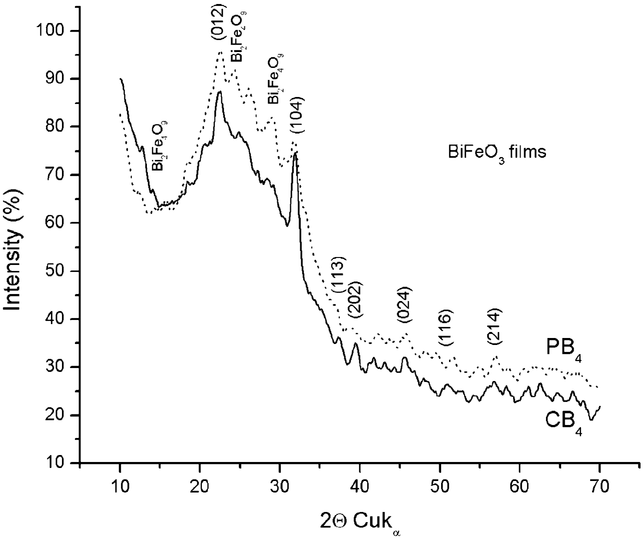

Fig. 1. XRD films patterns after 4 annealing treatment at 500 °C in air (CB_4, four layers with citric acid precursor solution and PB_4, four layers with polyvinyl alcohol precursor solution).

The structural and optical characterization of $BiFeO_3$ multilayer thin films was made by the Spectroscopic Ellipsometry. Owing to the fact that no n–k spectra were found in the literature as reference data, the $BiFeO_3$ samples were fitted assuming a physical homogeneous mixture of Bi_2O_3 and Fe_2O_3 oxides. It may be therefore expected equal volume fractions of Bi_2O_3 and Fe_2O_3 from the spectroellipsometric fitted data. It is noteworthy that a fit based on a $Bi_3Fe_5O_{12}$ reference was performed with no encouraging results.

The sample thickness and the volume fractions of the Bi_2O_3 and Fe_2O_3 mixture oxides are presented in Table 1 together with the fit error. The error reported in Table 1 was calculated

Table 1
Thickness of the samples (d) and the volume fraction of the components for C (citric acid precursor solution) and P (polyvinyl alcohol precursor solution) type samples

No. of layers	TT[a]	d (Å)		Bi_2O_3 (%)		Fe_2O_3-W (%)		Air (%)		Error × 10^{-7}	
		C type	P type	C type	P type	C type	P type	C type	P type	C type	P type
Bi	–	1970	1950	19.52	21.49	20.72	23.20	59.76	55.31	2630	11073
B1	1	1930	1480	20.08	17.81	21.10	33.14	58.82	49.05	4739	94774
B2	2	4670	4230	18.73	24.87	25.81	27.03	55.47	48.10	13732	56477
B3	3	7430	5360	21.46	27.27	25.07	43.48	53.46	29.25	22923	220130
B4	4	9570	7540	24.95	38.75	26.15	35.18	48.90	26.06	21262	212448

[a] TT, number of thermal treatments.

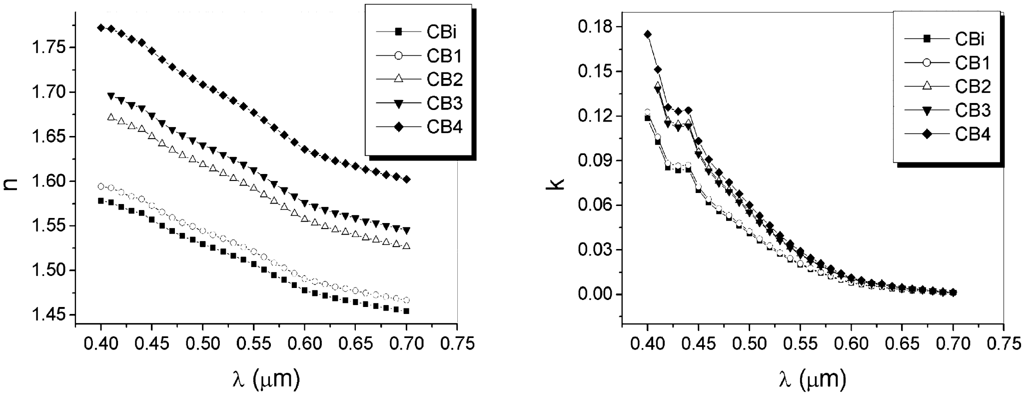

Fig. 2. The dispersion of the optical constants (*n*, *k*) of the $BiFeO_3$ films deposited on glass (samples CB, citric acid precursor solution).

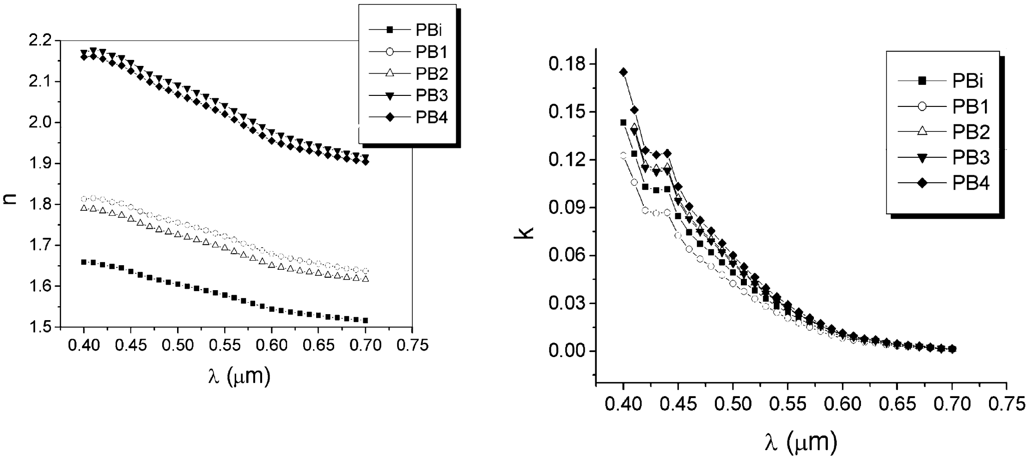

Fig. 3. The dispersion of the optical constants (*n*, *k*) of the $BiFeO_3$ films deposited on glass (samples PB, polyvinyl alcohol precursor solution).

according to Eq. (1):

$$\text{Error} = \sum_{i=1}^{N} \frac{(R_i^{\text{ec}} - R_i^{\text{em}})^2 + (I_i^{\text{mc}} - I_i^{\text{me}})^2}{N}, \tag{1}$$

with R_e is the real part of ellipsometric function ($\tan \text{PSI} \times \cos \text{DELTA}$), R_i^{ec} the calculated value, R_i^{em} the measured value, I_m the imaginary part of ellipsometric function ($\tan \text{PSI} \times \sin \text{DELTA}$), I_i^{mc} the calculated value, I_i^{me} the measured value, and N is the number of experimental points.

The thickness of the layers vary from 1500 to 10000 Å and increased with the number of depositions. Lower values were obtained in the case of polyvinyl alcohol based precursor solution (PB). The lower viscosity of the solution can explain this variation. On may conclude than the thickness of the films may be controlled by the nature of chelate agent and its concentration.

In Figs. 2 and 3 are presented the optical constants (*n*, *k*) of the samples obtained from the best fit. The curves of the refractive index rise towards short wavelength, showing the typical shape of a dispersion curve. On the other hand, the extinction coefficient curves showing a bunching behavior towards higher wavelengths.

The direct and the indirect optical bandgap, $E_\text{g}d$ (Eq. (2)), $E_\text{g}i$ (Eq. (3)), were calculated from Tauc[12] representations:

$$\alpha \sim \frac{1}{h\nu}(h\nu - E_\text{g}d)^{1/2}, \tag{2}$$

$$\alpha \sim \frac{1}{h\nu}(h\nu - E_\text{g}d)^{2}, \tag{3}$$

where α is the absorption coefficient, h the Plank's constant, $\nu = c/\lambda$, and $E_\text{g}d$, $E_\text{g}i$ are the direct and indirect optical gap. The results are presented in Fig. 4 and Table 2.

Table 2
Direct and indirect optical band gap for C (citric acid precursor solution) and P (polyvinyl alcohol precursor solution) type samples

No. of layers	$E_\text{g}d$ (eV)		$E_\text{g}i$ (eV)	
	C type	P type	C type	P type
Bi	2.78	2.70	1.84	1.84
B1	2.78	2.81	1.85	1.84
B2	2.62	2.78	1.84	1.85
B3	2.59	2.82	1.83	1.85
B4	2.67	2.81	1.84	1.85

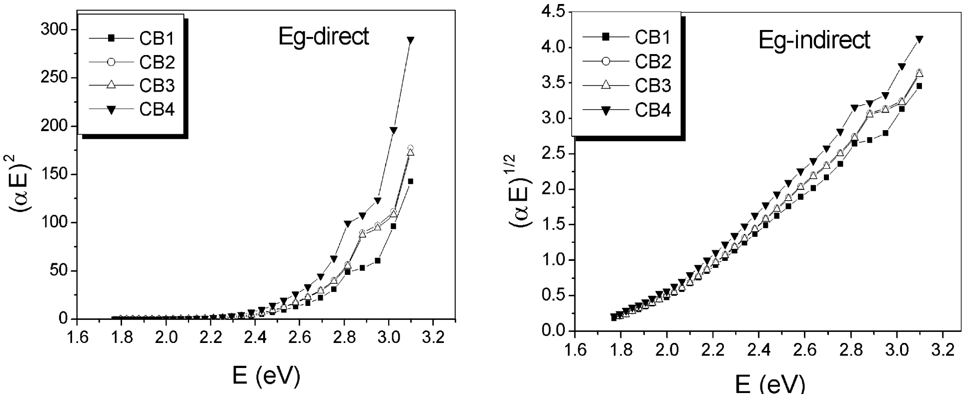

Fig. 4. Tauc representation for the optical band gap, direct (a) and indirect (b) for C type samples.

4. Conclusions

The present study is devoted to the synthesis and characterization of $BiFeO_3$ films. A wet chemical route, using two kinds of chelated agents – citric acid or polyvinyl alcohol – was adopted to obtain thin films. The thickness of the films can be controlled in a wide range.

The tendency of crystallization with the increasing number of layers and annealing treatments was noticed. Treatments at higher temperature are necessary.

Owing to the fact that no *n–k* spectra were found in the literature as reference data, the $BiFeO_3$ samples were fitted assuming a physical homogeneous mixture of Bi_2O_3 and Fe_2O_3 oxides. It may be therefore expected equal volume fractions of Bi_2O_3 and Fe_2O_3 from the spectroellipsometric fitted data. It is noteworthy that a fit based on a $Bi_3Fe_5O_{12}$ reference was performed with no encouraging results.

Detailed investigation on the compositions and microstructure of the films are in progress.

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