Materials Science-Poland, 29(1), 2011, pp. 41-46
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-011-0008-6

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Microwave dielectric properties of $BiFeO_3$ multiferoic films deposited on conductive layers*

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Nondoped $BiFeO_3$ (BFO) and doped $Bi_{0.9}La_{0.1}Fe_{0.9}Mn_{0.1}O_3$ (BLFMO) thin films (d = 200–350 nm) were grown at 650–750 °C by RF sputtering on Si and $SrTiO_3$(100), coated by conductive $LaNiO_3$ films and $La_{2/3}Ca_{1/3}MnO_3/SrRuO_3$ bilayers. The complex dielectric permittivity of the films was measured at room temperature in the frequency range from 10 MHz to 10 GHz using parallel plate capacitor structures. Dielectric properties of the polycrystalline BFO films were compared with those of the epitaxial quality BLFMO films, and it was seen that the latter has better microwave performance than the former. The dielectric losses were below 0.05 at 1 GHz frequency, which may be acceptable for microwave applications.

Keywords: *multiferroic, bismuth ferrite, RF sputtering, dielectric permittivity, dielectric loss*

1. Introduction

Ferroelectric ferromagnets with coupled electric, magnetic, and structural order parameters are known as multiferroics [1]. Electrical and magnetic properties of the materials may be controlled via applied electric and magnetic fields. Bismuth ferrite, $BiFeO_3$ (BFO) is one of the most extensively studied multiferroic materials. It is ferroelectric ($T_C \approx 1103$ K), antiferromagnetic ($T_N \approx 643$ K) and exhibits weak magnetism at room temperature due to a residual moment occurring from a canted spin structure [2]. The switchable polarization of BFO exceeds any other perovskite ferroelectric [3]. Electrical leakage resulting from possible defects and nonstoichiometry remains one of the main obstacles to the practical applications of the material, although it was found recently that the electrical conductivity of BFO could be reduced by partial substitution of both Bi and Fe ions [4, 5]. There is increasing interest in BFO thin films as promising candidate materials for advanced ferroelectric memory applications, as well as for the fabrication of sensors and new types of devices for spintronics. BFO also has a certain interest due to the observed emission of terahertz radiation, as was reported in [6]. Such emission could provide a very fast and non-destructive method for ferroelectric memory readout. Being insensitive to leakage and suitable for memory applications at such high frequencies, the material still should show appropriate dielectric loss characteristics. However, interpretation of dielectric permittivity, dielectric losses, and polarization remains rather complicated due to the relatively high conductivity of the material, and thus detailed investigations of BFO films in a wide frequency range are still of great interest.

*The paper was presented during the 6th International Conference on Microwave Materials and their Applications MMA-2010, September 1–3, 2010, Warszawa.

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Thin films of polycrystalline $BiFeO_3$/$LaNiO_3$/Si (BFO/LNO/Si) and La and Mn-doped $Bi_{0.9}La_{0.1}Fe_{0.9}Mn_{0.1}O_3$/$La_{2/3}Ca_{1/3}MnO_3$/$SrRuO_3$/$SrTiO_3$ (BLFMO/LSMO/SRO/STO) were grown for this work and their dielectric properties were characterized in a wide frequency range. Partial substitution of Bi by La and Fe by Mn was undertaken in order to stabilize the perovskite structure and to reduce the electrical conductivity of the multiferroic compound.

2. Experimental

BFO and BLFMO films with a thickness d ranging from about 200 nm to 350 nm were grown *in-situ* at 650–700 °C, under Ar/O_2 (1:1) gas at a pressure of 6–10 Pa, by RF magnetron sputtering. Wafers of n-type Si(111) coated with polycrystalline conductive $LaNiO_3$ layers were used for the preparation of the BFO films, while crystalline $SrTiO_3$(100) with heteroepitaxially grown, lattice-matched $La_{2/3}Ca_{1/3}MnO_3$/$SrRuO_3$ bilayer films were used as the substrates for BLFMO film growth. Disk-shaped ceramic targets of both undoped and La, Mn-doped BFO used in this work for film deposition were synthesized by applying a standard solid state reaction method using high purity powdered oxides. The Bi content in the targets was slightly enhanced (by about 5 %) to compensate possible loss of highly volatile Bi during film growth. The crystalline structure of the synthesized ceramic targets and the prepared thin films was investigated by measuring XRD spectra using CuKα radiation. The surface quality of the prepared films and their heterostructures were studied by performing AFM analysis. An AFM surface image of the as-prepared BFO films revealed a relatively smooth surface with an average grain size of about 12 nm and a surface roughness of about 9 nm. The relatively thick ($d \cong 20$ μm) ceramic BFO layers, used in this work for comparative studies over the low-frequency range, were prepared on Pt-coated Si(111) substrates by sedimentation of BFO powder coatings from ethyl alcohol-based suspensions. The prepared coatings of uniform thickness were further dried at room temperature and subsequently heated in air for 15 min at 850 °C. The dielectric properties of the prepared thick BFO layers were measured in the frequency range up to 200 MHz, using a computer controlled coaxial spectrometer. Silver paste applied to the top of the BFO film surface and Pt-coated substrates was used as the electrodes.

The Ti/Au layers with a thickness of about 250 nm were deposited on top of the thin films in order to perform further tests on the electrical contacts for microwave measurements. The gold electrodes, having the shape of circular patches, were patterned by a conventional wet lithography technique. Structures with a center electrode of various diameters were measured in order to eliminate parasitic capacitances. The high-frequency dielectric properties of the BFO films were measured using a vector network analyzer with a coplanar-waveguide probe. Impedance of the structure was measured by the one-port measurement technique. The dielectric permittivity and dielectric loss were obtained using a formula for a parallel-plate electrode condenser:

$$C^* = \frac{\varepsilon^*_{PPE}\varepsilon_0 S}{h} \tag{1}$$

where ε^*_{PPE} is the complex dielectric permittivity of BFO, ε_0 is the dielectric constant, S is the electrode area, h is the film thickness, and C^* is the capacitance calculated from the impedance data.

3. Results and Discussion

XRD $\Theta - 2\Theta$ spectra of the synthesized BFO ceramics (see Fig. 1) confirmed the presence of a rhombohedral structure having space group R3c, lattice parameter a_{rh} = 0.396 nm and α = 89.45°. A slightly lower value for the lattice parameter a_{rh} and a higher α value (0.395 nm and 89.45°) were indicated from the XRD spectra of the ceramic BLFMO samples. Thus, one can conclude that Bi in the doped material is partially substituted by La ions and the rhombohedral distortion is slightly reduced by doping with Mn.

The XRD spectra obtained for the undoped BFO/LNO films revealed the polycrystalline qual-

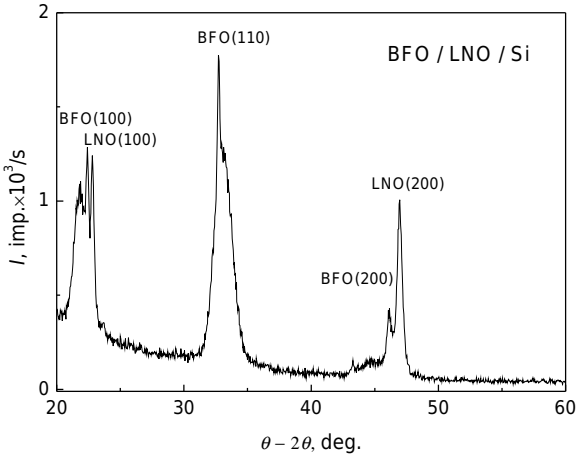

Fig. 1. $\Theta - 2\Theta$ X-ray diffraction (XRD) spectra measured for thin BFO films grown by magnetron sputtering on LNO-coated Si(111) substrates.

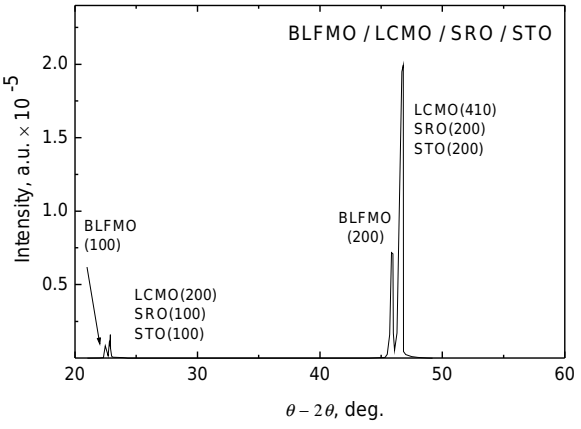

Fig. 2. $\Theta - 2\Theta$ scans of the $Bi_{0.9}La_{0.1}Fe_{0.9}Mn_{0.1}O_3$ film grown by RF magnetron sputtering on crystalline $SrTiO_3$ (100) substrates coated by a conductive lattice-matched $La_{2/3}Ca_{1/3}MnO_3$/ $SrRuO_3$ bilayer film.

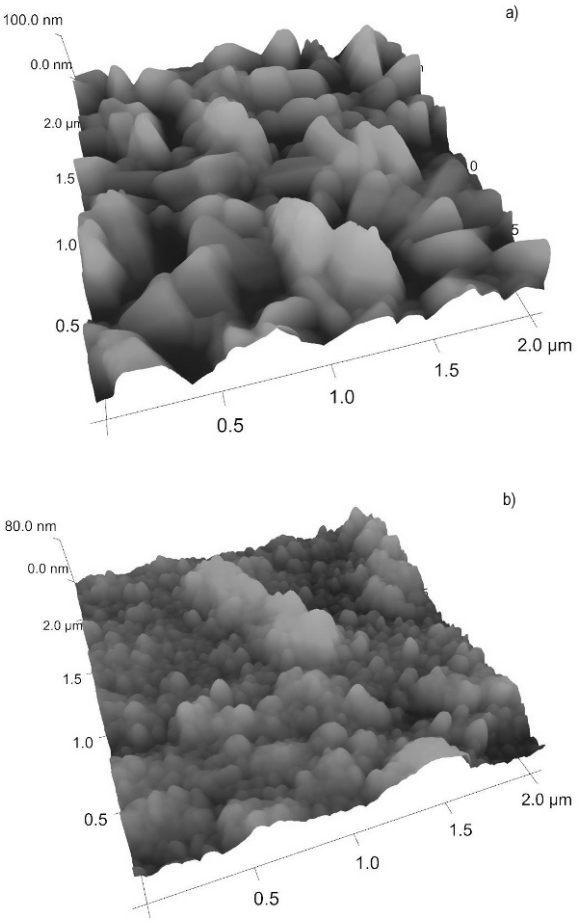

Fig. 3. Surface images of individual layers of the BLFMO/LCMO/SRO multilayered film, prepared by magnetron sputtering onto lattice-matched $SrTiO_3$(100) substrates: a) $Bi_{0.9}La_{0.1}Fe_{0.9}Mn_{0.1}O_3$ film, b) intermediate $La_{2/3}Ca_{1/3}MnO_3$ film. Take note of the different scales of the vertical axes.

ity of the BFO phase material, with negligible amount of impurity phase ($Bi_{36}Fe_2O_{57}$). Meanwhile, XRD reflexes of the BLFMO films grown on the lattice matched substrate (see Fig. 2) showed single phase high crystalline material with the off-plane lattice parameter of a pseudocubic unit cell of about 3.95 nm.

AFM surface image of the 350 nm BLFMO films grown on a lattice-matched LCMO/SRO/STO structure (see Fig. 3 a, b and Fig. 4) demonstrated relatively smooth surface with average grain size of about 200 nm and surface roughness of about 20 nm.

The dielectric constant of BFO ceramics was reported to vary between 30 and a few hundred, depending on the sample morphology and the frequency range [7–9]. Domain-wall motion and space-charges can contribute significantly to the measured permittivity value [10]. Therefore, the values around 100 at low frequencies in our samples far exceeded the clamped value of dielectric permittivity, which is below 40. Dielectric losses

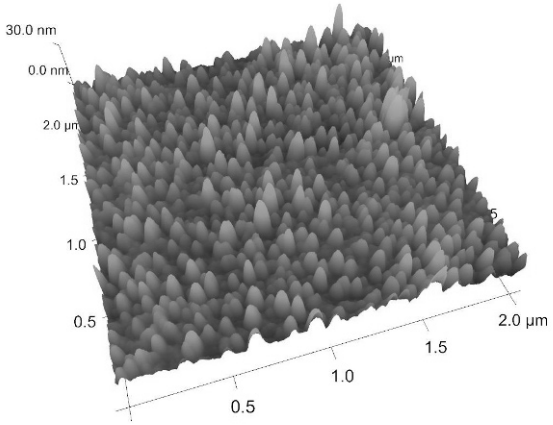

Fig. 4. Surface image of the underlying highly conductive $SrRuO_3$ layer in the BLFMO/LCMO/SRO multilayered film prepared by magnetron sputtering onto lattice-matched $SrTiO_3(100)$ substrates.

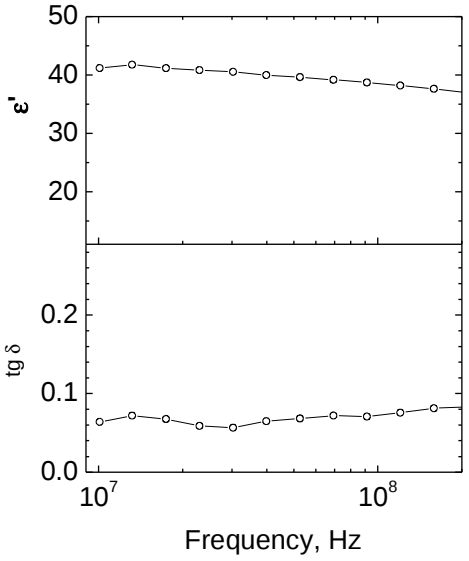

Fig. 5. The real part of the complex dielectric permittivity and tan δ of BFO thick film on Pt-coated Si(111) substrate at high frequencies.

in polycrystalline thick film were found to increase sharply as the frequency decreases, and therefore one can expect the investigated structures to exhibit noticeable DC conductivity. The dielectric permittivity and dielectric losses of thick BFO films are strongly influenced by relatively high conductivity at low frequencies, but at 1 MHz these losses are almost suppressed by frequency and reaches values below 0.1. Dielectric permittivity and losses of BFO in radio frequency region at room temperature are presented in Fig. 5. The dielectric permittivity changes only slightly when frequency is increasing by two decades. The variation is close to instrumental error of the coaxial spectrometer; however, a loss factor of 0.07 in the whole range suggests that a small dielectric dispersion possibly exists in this frequency range.

Results of the microwave dielectric measurements performed on 250 nm BFO thin films of polycrystalline quality deposited on n-Si(111) substrate with conductive $LaNiO_3$ as the top layer ($d \sim 200$ nm) are presented in Fig. 6. Circular patch capacitors with an upper Au electrode of 50 and 100 µm in diameter were formed so that they matched the 250 µm pitch coplanar G-S-G microprobes [11, 12]. Disk-shaped capacitor patches and surrounding metallization area, along with a bottom conductive LNO layer, were used as two serial capacitors for impedance measurements. The real part of the dielectric permittivity at frequencies in the lower part of the considered range is very close to that obtained for thick film using alternative measuring techniques. It decreases significantly as the frequency increases. The value of the dielectric loss remains constant up to a frequency of approximately 300 MHz. Although stable, such dielectric losses are higher compared with the values which usually characterize high quality materials used for microwave applications [13].

It is interesting to note that the loss tangent value for thin BFO film at low frequency is very similar to the estimated loss tangent value for ceramic film at a frequency above 107 Hz, as is seen in Fig. 5. Furthermore, the dielectric permittivity values are in a good agreement with the values obtained for BFO ceramics at frequencies in the microwave and terahertz range [9, 14].

Doping the BFO with La and Mn substantially increased the electric resistivity of the ceramic. The dielectric constant of BLFMO film maintained a more stable value in a wide frequency range compared with pure BFO 14 % decrease in the value of

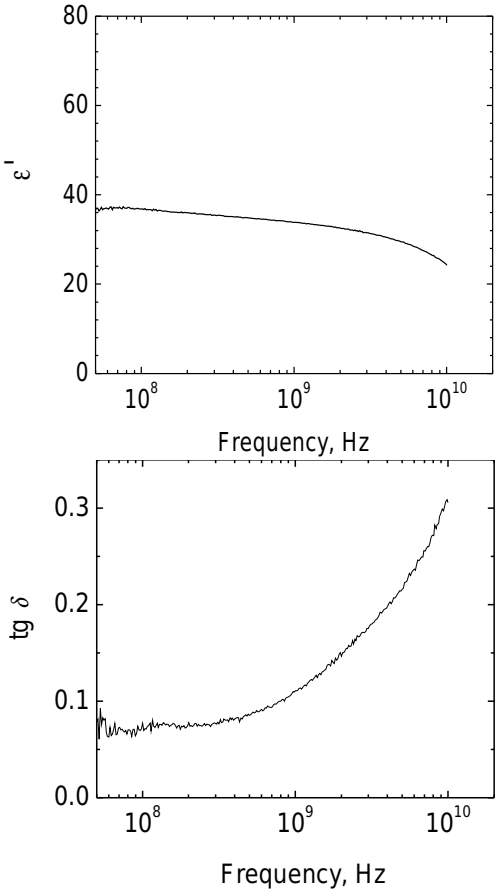

Fig. 6. Frequency-dependency of the real part of the complex dielectric permittivity and tan δ of BFO thin film on LNO/Si(111) substrate.

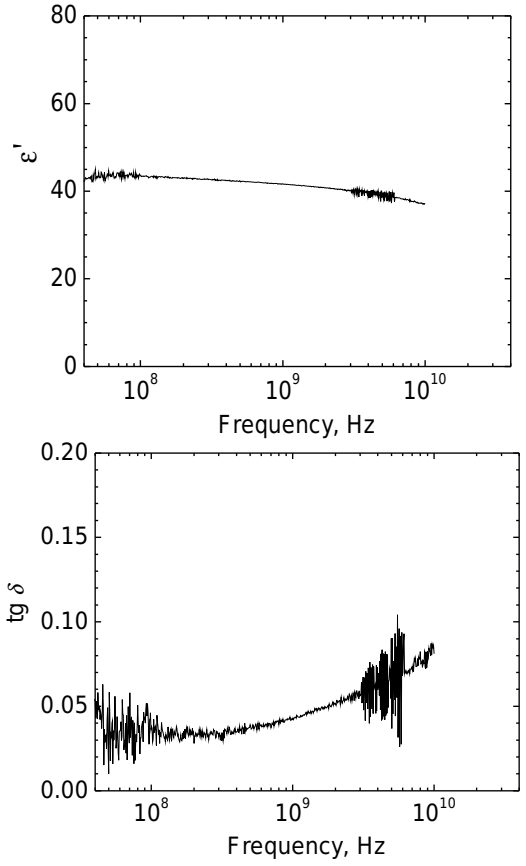

Fig. 7. Frequency-dependency of the real part of the complex dielectric permittivity and tan δ of BLFMO thin film on STO(100) substrate with LCMO/SRO buffer layer.

ε was found at frequencies from 40 MHz to 10 GHz (see Fig. 7). The loss tangent value is lower than 0.05 at 1 GHz frequency, which may be acceptable for microwave applications. Improvements to the interface of the electric contacts and to the geometry of the investigated structures may further improve the microwave properties of the doped BFO thin films.

4. Conclusions

The complex dielectric permittivity of multiferroic $BiFeO_3$ and $Bi_{0.9}La_{0.1}Fe_{0.9}Mn_{0.1}O_3$ thin films deposited on conducting substrates was investigated in a wide frequency range from 20 Hz to 10 GHz. Dielectric losses of 0.07 or higher characterize polycrystalline BFO films over a wide frequency range, i.e. from the microwave frequency range down to 1 MHz, where leakage currents start to dominate the dielectric response. Co-doping of bismuth ferrite by La and Mn increased the electric resistivity of the thin film. The epitaxial quality BLFMO deposited on a conductive LCMO/SRO bilayer showed dielectric losses not exceeding 0.05 at a frequency of 1 GHz, which may be acceptable for microwave applications.

Acknowledgements

This work was partially funded by grant No. MP-114/2010 provided by the Research Council of Lithuania.

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Received 13.09.2010
Accepted 13.09.2010