Microwave dielectric properties of $BiFeO_3$ thin film prepared by aqueous chemical solution deposition method#

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Received 24 April 2009; received in revised form 2 October 2009; accepted 7 November 2009

Abstract

We report high frequency dielectric properties of multiferroic $BiFeO_3$ (BFO) thin film deposited by means of aqueous chemical solution deposition on platinized silicon substrate. The structure analysis of the BFO performed by X-ray diffraction and energy dispersive analysis showed pure, single-phase quality of the thin films. The impedance measurements were performed by vector network analyzer in frequency range 100 MHz to 10 GHz at ambient temperature. The film leakage currents dominate dielectric losses at low frequencies. The dielectric constant of the film is around 40. An internal charged defects acting as energy traps for electrons dominate dielectric losses in the frequency region above 4 GHz.

Keywords*: multiferroic, chemical solution deposition, X-ray diffraction, dielectric permittivity*

I. Introduction

Due to their technological potential, increasing effort is devoted to studying multiferoic thin films. Bismuth iron oxide $BiFeO_3$ (BFO) is a promising material, because it has good ferroelectric properties, exhibits ferroelectricity and G-type antiferromagnetism with weak ferromagnetic order simultaneously and has a T_c at about 1100 K, higher than other ferroelectric materials [1]. It is considered as a substitute for $Pb(Zr,Ti)O_3$ family materials, whose toxicity due to the lead content is a serious drawback. However, BFO suffers from low electrical resistivity, preventing these materials from exhibiting essential polarization performance at room temperature. For reducing the electrical conduction of perovskite based ferroelectric thin films deposition technology improvements, such as controllable oxygen stoichiometry in the films were used. Substitution by rare-earth ions for reduction of oxygen vacancies, as material-design-like concept, was applied as well [2]. For thin film deposition various methods are used [2,3]. For deposition of BFO films in this work, the aqueous chemical solution deposition (CSD) was used. Chemical solution deposition, as compared with other method shows capability of large-area deposition, low cost and effectiveness. The use of only water as the solvent has ecologic and economic advantages compared to alkoxide or Pechini type CSD routes. Aqueous solutions of citratocomplexes of Bi(III) and Fe(III) are used and combined to obtain $BiFeO_3$ precursor solutions. The precursors are stable in ambient air, as the metal ions are stabilized against hydrolysis and condensation by the chelating ligands. Recently, it was shown that phase pure $BiFeO_3$ powders could be synthesized from these precursors [3] even though the synthesis of phase pure $BiFeO_3$ is reported to be challenging due to the complex phase diagram in the Bi_2O_3–Fe_2O_3 system. To this end, the precursors were thermally decomposed in dynamic dry air and annealed at 600°C. Furthermore, besides the possibility to form phase pure powders, the precursors allow deposition of uniform thin films on platinized silicon substrates, after the surface is rendered hydrophilic by an appro-

#Paper presented at *6th COST 539 Workshop, Advance Functional Characterization of Nanostructured Materials,* February 23-25, 2009, Madrid, Spain

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priate surface pretreatment. Here, we show the formation of phase pure $BiFeO_3$ films from the aqueous CSD route. Since this material is highly electrically conductive, interpretations of its static dielectric permittivity and polarization measurements are rather complicated, therefore investigations of the material in the wide frequency range were performed.

II. Experimental

The precursor synthesis and decomposition is described in detail elsewhere [4]. Bi(III) citrate is dissolved in water upon addition of concentration NH_3 up to pH 7 and stabilized with monoethanolamine [5]. Fe(III) citrate is dissolved in water. Mixing of these monometal ion solutions and pH adjustment to 7 yielded the $BiFeO_3$ precursor solution of 0.6 mol/l concentration. The solutions are deposited by spin coating onto platinized silicon pieces (2.5×2.5 cm^2), cleaned with sulfuric acid/peroxide and ammonia/peroxide mixtures to obtain a hydrophilic surface [6]. To get films homogeneous in thickness three layers were obtained by subsequent spincoating and stepwise thermal treatment on hot plates with increasing temperatures (160 – 260 – 480°C), intermediately and finally annealed at 600°C in a preheated tube furnace applying flowing dry air (0.5 l/min). The processing is very sensitive and requires careful control in order to obtain phase purity. The BFO thin films with thickness of 74 nm were deposited on $Pt/TiO_2/SiO_2/(100)Si$ substrates with 80 nm thick Pt top layer.

The dielectric properties of BFO thin films were measured by a vector network analyzer Agilent E8363 with ground-signal-ground miniature wafer probe using one-port measurement technique described elsewhere [7]. For microwave measurements an additional metallic layer of 150 nm thickness was deposited on the top of the film. The golden electrodes in the shape of circular patches were structured in the top metallic layer by lift-off to get microwave parallel plate capacitor structures surrounded by large area metallic film. That surrounding mettalic film forms outer condenser with big capacitance which is used for high-frequency electrical shorting of top contacts with bottom Pt layer. That allows measurements of the dielectric permittivity and loss using parallel-plate electrode condenser formula

$$C^*_{PPE}(\omega) = \varepsilon^*(\omega)\, \varepsilon_0 \pi a^2/h \qquad (1)$$

where ε^* is complex dielectric permittivity of BFO, ε_0=8.85×10^{-12} F/m is the dielectric constant of free space, a is radius of the circular electrode patch, h is the film thickness, and C^* is the capacitance calculated from the impedance data. Use of different diameter patches allows elimination of the parasitics of outer condenser and effects of series resistance introduced by Pt layer which interconnects the inner circular and outer capacitors [7]. The probe with 250 μm patch was used to measure 50 and 100 μm diameter patches. The measurements were made at a temperature of 297 K.

III. Results and discussion

SEM secondary and backscattering electron (BSE) analysis was employed to examine the surface of the films before depositing the upper metallic layer depositing. The films are characterized by a relatively small grain size and homogeneous surface. An SEM backscattering electron image of the BFO film surface is shown in Fig. 1.

There is no sign of any phase segregation from the BSE image. Energy dispersive X-ray analysis (EDX) results are presented in Fig. 2. They showed no impurities in the film. Peaks for O, Bi, Fe and Pt, which is related to substrate, were detected. Investigation of X-ray diffraction (XRD) patterns revealed the single-phase rhombohedral BFO films structure. The XRD pattern of the grown $BiFeO_3$ is shown in Fig. 3. It can be concluded from the combined information from SEM and XRD that the film is phase pure without any substantial amount of foreign metal contaminations.

The dielectric properties were investigated by measuring the thin films in parallel plate capacitor configuration. Low frequency measurements performed with capacitance bridge showed high conductivity of the samples. That did not allow estimation of the real dielectric constant of the material. It is known that parasitic phase of Fe or Bi oxides and formation of oxygen vacancies can be the origin of high conductivity in pure bulk and thin film BFO [8,9]. The increase of the measurement frequency usually allows eliminating the ionic conductivity effects to the dielectric spectra. The results for dielectric permittivity measurements at

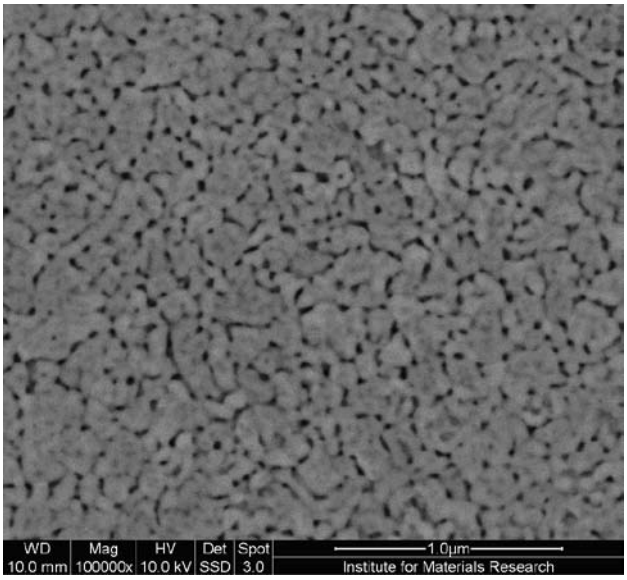

Figure 1. SEM backscattering electron image of surface of BFO thin film grown by aqueous CSD method

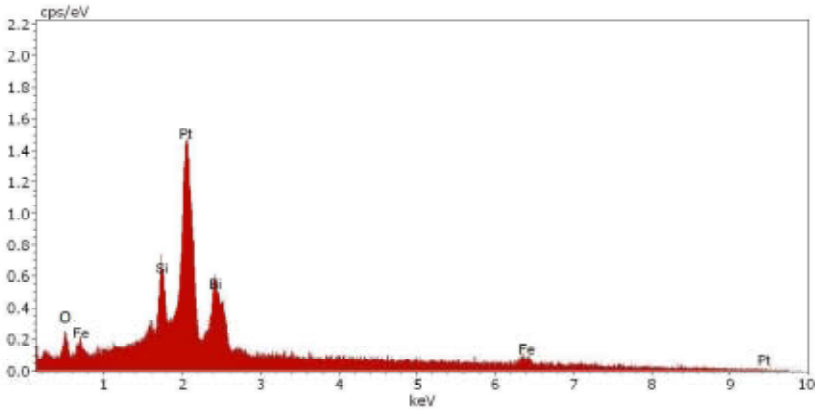

Figure 2. EDX analysis results for BFO thin film

high frequencies are shown in Fig. 4. At the low-frequency side of the spectrum, the dielectric losses probably reflect external charged defects dominated leakage current. The straight line is fit to measurement data by the DC conductivity formula

$$\sigma_{DC} = \varepsilon'' \varepsilon_0 \omega \qquad (2)$$

where ε'' is dielectric losses, ε_0 is the permittivity of free space and ω is the circle frequency. The frequency independent part of conductivity gives σ_{DC} = 0.365 S·m^{-1}. At frequencies above 1 GHz strong increase in conductivity marks beginning of alternating (AC) conductivity and real dielectric relaxation process starts to dominate. It is interesting to note that the real part of the dielectric permittivity changes only very slightly with frequency in the lower part of the spectrum and its value is near 40. On the one hand, such value is lower as compared to recently reported results for ceramics samples at few megahertz frequency [9], and can be explained by a number of factors, such as defects in the film, at the interfaces, and due to the strains. Often the interdiffusion, chemical reactions and structural defects at the interfaces are described as dead layers and they may be the reason for a reduced film permittivity. On the other hand, even lower value for BFO ceramics was reported by terahertz frequency spectroscopic studies [10]. The decrease in the dielectric permittivity above 5 GHz frequency is an effect of serial resistances of electrodes. It can be corrected by de-embedding of series-resistances during the impedance measurements.

The frequency dependence of loss tangent of BFO thin film is shown in Fig. 5. The effect of the contact resistance between the probe and the gold plate of the thin film capacitor was taken into account also using a serial circuit scheme. The value for serial resistance introduced by the probe contact normally would not exceed 0.5 Ω. This value we used for correction of tangent delta and the result is presented by open circles in Fig. 5. Though reduced, the dielectric losses at microwaves remain high as compared with the bulk BFO

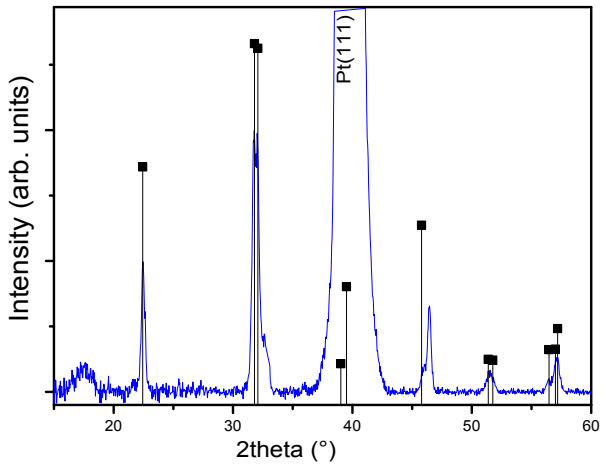

Figure 3. X-ray diffraction pattern of the BFO thin film. Solid rectangulars show $BiFeO_3$ contribution to the pattern

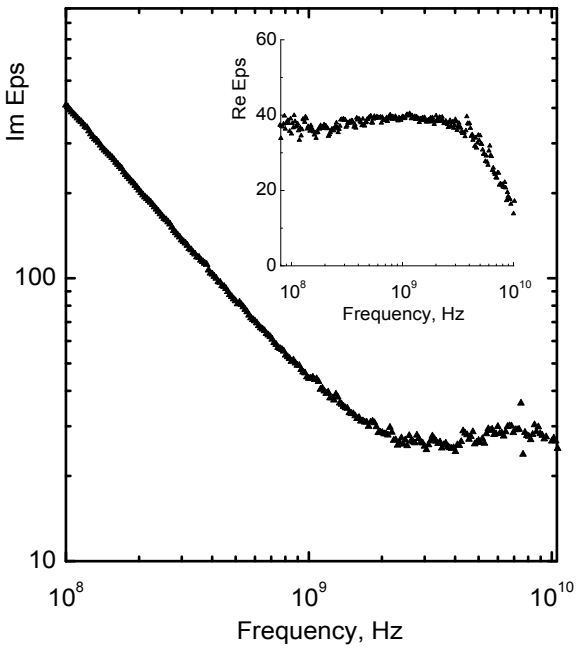

Figure 4. Frequency dependences of real part (insert) and imaginary parts of the dielectric permittivity for BFO thin film

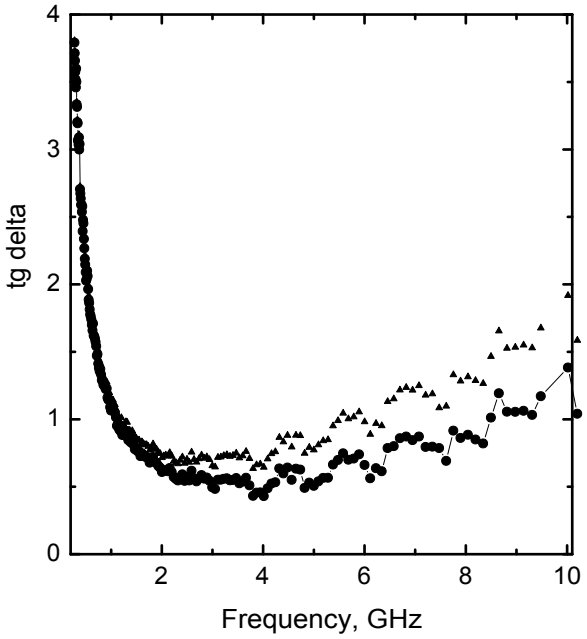

Figure 5. Frequency dependences of dielectric losses for BFO thin film. Dark circles mark losses then resistance R_c= 0.5 Ω between top contact and probe is accounted

samples. The loss tangent decreases with frequency until 0.5 at 4 GHz. Such losses are considerably higher as compared to the intrinsic phonon-related losses for materials outside phase transition region [10]. Away from the resonant peaks, the loss tangent increases with frequency in the microwave region. The most probable cause for such high increasing loss tangent is the presence of charged defects. The loss tangent associated with the charged defects is proportional to the frequency in perovskite crystals. In the investigated films, the internal charged defects are related to oxygen vacancies. They act as energy traps for electrons. Since BFO is in the ferroelectric state at room temperature, the charged defects can be pinned to the ferroelectric domain walls. Therefore, along with the external defects, they have a significant influence on the dielectric properties of BFO in whole frequency region investigated.

IV. Conclusions

The multiferroic $BiFeO_3$ thin films were grown by means of aqueous chemical solution deposition on platinized silicon substrates. The structure of the BFO thin film was investigated at room temperature by X-ray diffraction and X-ray energy dispersive analysis that showed pure rhombohedral phase. Scanning electron microscopy analysis confirmed the contiguous character of the surface of the films. The impedance measurements were performed using vector network analyzer in radio and microwave region at room temperature. The dielectric constant was found to be 40. The leakage currents dominate dielectric losses at low frequencies. Loss tangent has the minimum value of 0.5 at approximately 4 GHz and increases with frequency. Oxygen vacancies related internal charged defects, which can be pinned to ferroelectric domains of BFO, act as energy traps for electrons and along with external defects of the thin film most probably contribute to dielectric losses in the whole microwave frequency region investigated.

Acknowledgment: This work was supported by COST 539 project and Lithuanian Science and Study Foundation project "MULTIMA". A. Hardy and M.K. Van Bael are postdoctoral research fellows of the Research Foundation Flanders (FWO-Vlaanderen).

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