Interfacial effects on the electrical properties of multiferroic BiFeO$_3$/Pt/Si thin film heterostructures

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Abstract

Polycrystalline BiFeO$_3$ thin films of various thickness were fabricated on (111)Pt/Ti/SiO$_2$/Si substrates via chemical solution deposition. The electrical properties were investigated using impedance and leakage current measurements. X-ray photoelectron spectroscopy (XPS) combined with Ar ion milling (depth profiling) was used to investigate elemental distribution near the electrode–film interface. It is shown that the dielectric constant depends on film thickness due to the presence of an interfacial film–electrode layer evidenced by XPS investigation. Direct current conductivity is found to be governed by Schottky and/or Poole-Frenkel mechanisms.

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1. Introduction

The structural and electrophysical properties of bismuth ferrite (BiFeO$_3$) have been investigated during the last decades due to simultaneous presence of ferroelectricity and antiferromagnetic order with weak ferromagnetism in this material [1–5]. Bismuth ferrite belongs to perovskite class of complex oxides with rhombohedrally distorted cell that can be described by the polar R$3c$ space group. Apart from the fact that the properties and magnetic structure of BiFeO$_3$ are of great interest from fundamental point of view [6,7], the possibility to create new electronic devices is also discussed [8]. In the last years, particular attention has been paid to BiFeO$_3$ thin films [9–13] since they allow direct integration of the material into up-to-date semiconductor technology. Successful fabrication of epitaxial [9] and polycrystalline [10–13] thin films has been reported.

A distinctive feature of ferroelectric thin films is the dependence of dielectric properties on film thickness. A number of experimental results published show that the dielectric constant of the films decreases with film thickness. For example, Paek et al. [14] reported some degradation of dielectric and leakage properties of BST ((Ba,Sr)TiO$_3$, barium strontium titanate) thin films of thickness ranging from 50 to 300 nm deposited on platinum electrode. They reported high resolution transmission electron microscopy investigations of a very thin layer (of thickness between 9.5 and 11 nm) with crystallinity different from that of the bulk film. This layer is claimed to have a significantly lower dielectric constant, and to contain a high concentration of defects (which, in turn, serve as an effective trap centre for mobile charges and domain walls). Such a layer has been made responsible for the thickness dependence of the dielectric properties, especially for very thin films (thinner than 200 nm). It is thought that the formation of dead layers occurs rather at film–bottom electrode interface than film–top electrode interface since the former is exposed to high temperature during film fabrication.
Leakage current properties constitute another critical aspect limiting the applicability of ferroelectric thin films in electronic devices. A profuse literature has been devoted to the analysis of leakage currents in ferroelectric thin films. The basic conduction mechanisms in dielectric films together with an exhaustive literature review can be found in textbooks [15,16]. Following Scott [15], different mechanisms including Schottky currents and quantum mechanical Fowler-Nordheim currents (surface-limited), as well as Poole-Frenkel and Space-Charge-Limited Currents (bulk-limited) can all be present in the same temperature and/or voltage ranges [15].

Analysis of the literature shows that dielectric and leakage current properties of ferroelectric thin films were mainly investigated on PZT (lead zirconate titanate), BST and SrTiO₃, and were not addressed for BiFeO₃. In view of growing practical importance of multiferroic materials (especially in the form of thin films), attempt is made in this work to systematically study the dielectric and leakage current properties of chemical solution deposited BiFeO₃ thin films, and to understand the mechanisms of electrical conductivity. Additionally, the results of XPS analysis (X-ray photoelectron spectroscopy) together with depth profiling are presented and discussed with emphasis on interfacial composition and interface formation between Pt bottom electrode and BiFeO₃ film.

2. Experimental details

Bi-acetate and Fe-acetylacetonate were weighted according to Bi₁.₀₂FeO₃ stoichiometry and dissolved in 1:2 mixture of deionized water and acetic acid. The final concentration of the precursor solution was 0.25 mol/l. Thin films were spin-coated at 5000 rpm for 30 s on commercial (111)Pt/Ti/SiO₂/Si substrates. Each layer was dried on a hot plate at 140 °C–150 °C and subsequently at 210 °C–235 °C for 5 min. In order to prevent cracking and peeling, the films were intermittently annealed in a pre-heated tube furnace in oxygen flow or in air at 650 °C for 10 min after each third layer deposition. Films consisting of 6, 9, 12 and 15 coatings were deposited. The samples were finally annealed at 650 °C for 1 h in oxygen or air.

The microstructures were observed using AFM (atomic force microscope, non-contact mode). Additionally, a one-coating specimen processed under the same conditions as above was prepared for XPS analysis. XPS characterization was conducted on Omicron Full Lab System. Ar ion sputtering (3 keV) served for depth profiling of the elemental composition. In order to suppress the radiation from the sample near edge, the peripheral part of the surface area was covered with a tantalum foil. The sputter rate was obtained from profilometric measurements of the Ar ion etched step. Systematic shifts of the XPS spectra (due to surface charging effect) were corrected using the 4f lines of Pt.

For electrical characterization, Pt and Au were sputtered on the films considered for electrical measurements (6, 9, 12 and 15 coatings) through a shadow mask one after another to get round electrodes of 0.6 mm diameter. Post top electrode deposition annealing was made at 400–450 °C for 15 min in air. The frequency-dependent conductivity and dielectric properties of the films were measured at room temperature at alternating driving signal amplitude of 25 mV using a computer-controlled Agilent 4192A impedance analyzer. Time–voltage- and temperature-dependent leakage currents were measured using a high-precision electrometer (Keithley 6517A). Current density–voltage (J–V) characteristics were acquired in the step mode with a delay time from 30 s to 200 s. The signal was applied to the bottom electrode in all cases. The temperature was measured with a thermocouple placed on the sample surface. Heating was performed using computer controlled heating stage which allows temperature control with an accuracy of 0.2 K.

3. Results and discussions

3.1. Microstructure and phase content

XRD (X-ray diffraction) and AFM analysis revealed that the films crystallized into the perovskite phase with (100) preferentially oriented grains (pseudocubic). The ellipsometric film thickness was 100 nm, 175 nm, 270 nm and 365 nm for the specimens consisting of 6, 9, 12 and 15 coatings, respectively. Microstructural aspects of chemical-solution-derived BiFeO₃ thin films annealed in different atmospheres are discussed in more details in our earlier paper [13]. In the present paper an AFM micrograph of the 365 nm thick film specimen is presented exemplary (Fig. 1). Uniform, dense and crack-free surface morphology is observed for all specimens investigated. Very similar morphologies were observed for the thinner films, though they were found to be smoother with a finer grain size.

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Fig. 1. AFM micrograph of BiFeO₃ thin film consisting of 15 coatings and annealed in flowing oxygen.
3.2. Dielectric properties

The specimens annealed in air were found to possess very high conductivity and hence could not be used for electrical characterization due to device limitation. In contrast, specimens treated in flowing oxygen were found to exhibit resistivity values several orders of magnitude higher. Therefore, in the following only specimens treated in oxygen are considered.

The room-temperature values of the real part of the dielectric constant, $\varepsilon'$ (dielectric constant in the following) of the specimens investigated are plotted vs. frequency, $f$, in Fig. 2. The fit of the data to the Curie-von Schweidler relation, $\varepsilon' \sim \omega^{a-1}$ ($\omega$ is the angular frequency) gives a frequency exponent, $a$, very close to unit ($a=0.995$) [13], which indicates that the dielectric constant is almost frequency-independent in the frequency range investigated.

The observed degradation of the dielectric constant (Fig. 2) with decreasing film thickness is in general agreement with the results reported earlier for BST and PZT films [14,17]. A simple two-layer model has been proposed to explain the thickness-dependence of the capacitance. This model takes into account a disturbed film-electrode interfacial layer and adjacent bulk, and can be expressed as follows [18]:

$$\frac{1}{C_m} = \frac{1}{C_b} + \frac{1}{C_i} = \frac{d_b}{\varepsilon_0 \varepsilon_b A} + \frac{1}{C_i}$$ \hspace{1cm} (1)

where $C_b$ if the “bulk” capacitance (distinct from the interfacial capacitance, $C_i$); $d_b$ represents the thickness of the ferroelectric film; $\varepsilon_0$ and $\varepsilon_b$ are the permittivity of free space and dielectric constant of the ferroelectric bulk, respectively; $A$ is the area of the capacitor. It is usually assumed that the thickness of the interfacial layer is negligibly small compared to thickness $d$ and hence $d \approx d_b$. Room-temperature values of the reciprocal of $C_m$ selected for $f=1$ kHz are plotted vs. film thickness in Fig. 3. The results of the fit to the two-layer model described by Eq. (1) are represented as straight lines. It must be stressed that the two-layer model has only a limited applicability in the case of very thin films (100 nm and below), i.e. the condition $d \approx d_b$ (or $d_i << d$, $d_i$ is the thickness of the interfacial layer) is no more fulfilled. Indeed, one can see the deviation of the point corresponding to $d=100$ nm from the linear dependence of $1/C_m$ vs. $d$, observed for thicker films (Fig. 3). The intrinsic dielectric constant and the interfacial capacitance obtained from the linear fit to Eq. (1), considering only the data of thicker films (solid line), are 98 and 23 nF, respectively. The question then arises as to the nature of the interfacial layer. It is known that Bi violently reacts with Pt (p. 151 in Ref. [15]), which constitutes the main disadvantage of using Pt bottom electrode for Bi-based thin films. Moreover, analysis of the Bi–Pt and Fe–Pt phase diagrams shows that Pt–Fe intermetallic compounds can also be stable in the temperature range considered. We suppose that in the particular case of BiFeO$_3$ thin films deposited on platinized silicon substrate, the intermetallic compounds mainly constitute the interfacial layer. These compounds are usually characterized by slightly higher resistance (ordered phase) compared to Pt, and the thickness-dependent properties of BiFeO$_3$ films (particularly, the abrupt drop of $\varepsilon'$ when $d$ decreases) are mainly due to the presence of these phases (see below for XPS analysis).

3.3. Leakage currents

Fig. 4 shows the time-dependent leakage current density ($J(t)$) measured at 0.3 V, 1 V, 1.5 V and 3 V and at room temperature for the 175 nm thick film. The $J(t)$ dependence is characteristic of dielectric relaxation following quasi steady-state true leakage current [17,19]. Increasing the applied voltage resulted in long-term degradation and electrical break-down as illustrated in the inset of Fig. 4. For a proper analysis of conduction mechanisms, the voltage, temperature and delay time regions where contributions of the currents due to dielectric relaxation can be neglected must be found. The conditions under which long-
term degradation was not observed were a delay time of 30 s, a maximum temperature of 100 °C and a maximum applied field of 80 kV/cm. The dependence of $J$ on film thickness at constant voltage and temperature is shown in Fig. 5. The thickness exponent of 0.88 obtained from the log $J$–log $d$ plot demonstrates that the leakage current density weakly depends on film thickness. The space-charge-limited current mechanism, which strongly depends on thickness, following the Mott-Gurney law (p. 86 in Ref.[15]):

$$J = \text{constant} \frac{V^2}{d^m}$$

or the generalized law [20]:

$$J = \text{constant} \frac{V^n}{d^m}$$

(2) (3)

where $n$ and $m$ are the arbitrary constants) can therefore be ruled out. The results indicate rather ohmic (note that $m$ is close to unit), Poole-Frenkel and/or interface limited (Schottky or tunnelling injection) leakage current mechanisms. Conclusions about the conduction mechanisms prevailing under certain conditions (temperature and bias voltage) are usually done based on the analysis of the shape and the character of $J$–$V$ dependencies. Following the Schottky mechanism,

$$J = A^* T^2 \exp \left( -\frac{e\phi_B}{k_B T} \right) \exp \left( \frac{eE}{4\pi\varepsilon} \right)^{1/2} \frac{e}{k_B T}$$

(4)

where $A^*$ is the effective Richardson coefficient, $e$ is the charge of electron, $T$ the absolute temperature, $\phi_B$ the Schottky barrier height, $\varepsilon$ the optical frequency dielectric constant and $k_B$ the Boltzmann constant. Linear plot of log$(J/T^2)$ vs. $V^{1/2}$ shall be obtained. The Poole-Frenkel mechanism:

$$J \exp \left( -q \left( \phi_B - \frac{\sqrt{qE/\pi\varepsilon}}{k_B T} \right) \right)$$

(5)

is characterized by a linear dependence of log$(J/E)$ plotted vs. $V^{1/2}$, and tunnelling injection gives a linear dependence of log$J/V^2$ vs. $V^{1/2}$ coordinates (see p. 403 in Ref. [16] for basic conduction mechanisms and their voltage and temperature dependencies). However the latter mechanism can be ruled out since it is temperature independent. Fig. 6 shows the $J$–$V$ characteristics measured at various temperatures for

![Fig. 4. Time dependence of leakage current measured at room temperature for a 175 nm thick (nine layers) BiFeO₃ thin film. The inset clearly shows long-term degradation process at 3 V followed by electrical break-down.](image)

![Fig. 5. Room temperature values of the leakage current density measured at 1 V and plotted vs. film thickness. Solid line shows the results of the linear fit. The graph demonstrates rather weak thickness dependence of the leakage current density with a thickness exponent of $m=0.88$ (see text).](image)

![Fig. 6. The leakage current data obtained for 270 nm BiFeO₃ film at various temperatures. The experimental results are represented in the Schottky coordinates ($J/T^2$ vs. $V^{1/2}$), (a) negative portion of the $J$–$V$ curve, i.e. negative voltage is applied to the bottom electrode, and (b) positive portion.](image)
the 270 nm BiFeO$_3$ film. The data are plotted in Schottky coordinates. At low temperature and voltage, the data can be well approximated to the classical Schottky model (Fig. 6a and b). Very similar $J-V$ dependencies were observed considering Poole-Frenkel model of conductivity ($\log(J/E)$ vs. $V^{1/2}$), Fig. 7. Activation energies of the conductivity, $E_a$, at various applied biases were found from linear fit to the $\log(J/T^2)$ vs. $T^{-1}$ and $\log(J/E)$ vs. $T^{-1}$ dependencies (not presented), considering Schottky and Poole-Frenkel models of conductivity, respectively. Fig. 8 shows how the activation energy correlates with applied bias voltage. The very weak field-dependence of $E_a$ (and, in turn, the barrier height, $\phi_B$) at lower voltages can be explained in terms of the high density of trapped charges. The barrier properties are, therefore, mainly determined by these charges rather than applied bias field [16]. Further increase of bias voltage leads to the reduction of the activation energy illustrated in Fig. 8. The linear fits of the corresponding portions of the curves allow a Schottky barrier height of 1.45 eV to be calculated. A Poole-Frenkel trap height is found to be 1.51 eV. This value corresponds to the ionization energy of traps located rather in the middle of forbidden gap. It must be mentioned however that based on these results we still cannot separate Schottky and Poole-Frenkel mechanisms of conductivity in our samples and both models must be taken into the account.

3.4. XPS characterization

In order to gain insight into substrate–film interface formation, its chemistry, and so to understand the results depicted above, XPS analysis together with depth profiling
were conducted on a one-layer film annealed in oxygen-rich atmosphere. The XPS spectra selected for various milling times or depths are shown in Fig. 9a. The XPS spectrum obtained on the as-processed film is also presented (dashed line). A small amount of carbon was detected for the as-processed specimen. Since the 1s peak of carbon disappeared after the first Ar⁺ milling run, we attribute it to surface contamination. Fig. 9b represents the variation of composition through film thickness. The dashed area shows the position of the film–electrode interface expected considering both ellipsometric and profilometric measurements. First, it should be mentioned that the specimen is slightly depleted in Bi and Fe with respect to oxygen, compared to stoichiometric composition. It can also be seen that the near-surface region is enriched with Bi with respect to Fe, which may indicate the segregation of Bi or most probably Bi₂O₃ on the sample surface. Some important information can also be obtained from peak position. A close look at the spectrum corresponding to the as-processed film (Fig. 9a) reveals that the Bi 4d and 4f peaks are systematically shifted to higher binding energies. This is an additional evidence of Bi₂O₃ surface segregation [21] (however, the possibility to modify the oxidation state of Bi by X-rays must not be excluded). The results obtained from depth profiling reveal that annealing at 650 °C for 1 h leads to substantial interdiffusion at the film–substrate interface, which consequently results in the deviation from stoichiometry mentioned above, and a wide interface. As the area in the vicinity of the bottom electrode–film interface is depleted in oxygen, the formation of Pt–Fe and Pt–Bi intermetallic compounds with varying Pt content is envisageable.

4. Conclusions

In conclusion, the dielectric and leakage current properties of chemical-solution-deposited multiferroic BiFeO₃ thin films have been investigated. The dielectric constant was found to be sensitive to film thickness. A two-layer model of two capacitance in series was applied to describe the results. An apparent dielectric constant of 98 and an interfacial capacitance of 23 nF were extracted for the linear dependence of the reciprocal capacitance on film thickness. The results of leakage current measurements are shown to be weakly thickness-dependent. Schottky or Poole-Frenkel mechanisms are advanced as possible conduction mechanisms. The electrical properties are correlated to substrate–film interface formation. XPS analysis shows a wide film–electrode interface due to interdiffusion. The character of elemental distribution points to the formation of Pt–Bi and Pt–Fe intermetallic compounds at the bottom electrode–film interface. The presence of these phases as well as the related disturbance of film stoichiometry are thought to determine the electrical properties of solution deposited BiFeO₃ films on Pt-electrodes.

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