

Capacitive field-effect pH sensor based on an electrolyte-ferroelectric-insulator-semiconductor structure

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1. Introduction

Current interest in perovskite and perovskite-related ferroelectric materials is based on their wide range of electrical properties ranging from insulating materials, ionic and/or electronic conductors up to p- and n-type semiconductors and superconductors. Perovskite oxides of the system $A_{1-x}A_x'BO_{3-b}$ ($A=Pb, Ba, La, Li$; $A'=Sr, Ca$; $B=Ti, Ta, Co, Fe$, etc.) are used in high density dynamic random access memories (DRAM), non-volatile ferroelectric random access memories (FeRAM), ferroelectric field-effect transistors, voltage-tuneable capacitors (varactors), optical memories and electro-optic modulators, solid-oxide fuel cells, etc. [1-4]. In addition, due to the presence of oxygen vacancies and ionic conductivity, perovskite oxides have a high catalytic activity to oxygen reduction and oxidation and thus, are suitable for a large variety of gas and vapour sensor applications. Examples of realised devices include sensors sensitive to carbon monoxide and hydrocarbon [5], ethanol [6,7], acetone [7], humidity [8], etc.

(Bio-)chemical sensors are widely used as powerful analytical tools in medical diagnostics, food industry, environmental monitoring, security and defence fields, etc. Exploring new materials for the high sensitive and efficient transduction of (bio-)chemical signals into a quantifiable electronic signal is of importance in biosensor research and technology. Due to the multifunctional material properties as well as the high catalytic activity and large dielectric constant, perovskite-oxide ferroelectrics represent a very attractive alternative material for the creation of chemical sensors and biosensors for liquids. While the unique dielectric, piezoelectric, pyroelectric, microwave and electro-optic properties of ferroelectrics have been well studied [1-4], to our knowledge, very little is known about the behaviour of high-k ferroelectric thin-films in electrolyte solutions [9-11].

In the present work, a pH sensor based on a field-effect capacitive EFIS (electrolyte-ferroelectric-insulator-semiconductor) structure with a thin-film perovskite-oxide gate of $Ba_xSr_{1-x}TiO_3$ (BST) composition prepared by means of pulsed laser deposition (PLD) technique has been realised and investigated for the first time. A high-temperature self-propagating synthesis (SHS) was used for the fabrication of the BST targets. In contrast to the conventional high-temperature ceramic technology, the SHS method is simple, ecologically clean, waste-less, energy-saving, high productive and cost-effective.

2. Synthesis of BST materials by SHS technique

Perovskite oxides of different composition ($Ba_{0.31}Sr_{0.69}TiO_3$ and $Ba_{0.25}Sr_{0.75}TiO_3$) have been synthesised using the SHS technological equipment that is schematically shown in Fig. 1 [12-14]. In the SHS process, a highly exothermic combustion of a powder mixture is locally initiated from the sample surface by means of a heat flux. After initiation, the reaction proceeds in the mode of self-propagation, resulting in a formation of a high-temperature front that propagates and transforms the reactants into products [15-17].

The high temperature developed in a combustion wave provides the complete conversion of the initial materials into the final high-quality product with a minimal amount of impurities due to the so-called self-purification processes. Moreover, the high velocity of processes provides a short synthesis time. In addition, by variation of the initial mixture components and the combustion conditions, it is possible to produce multi-phase materials with a given chemical and phase composition as well as to control their microstructure and properties. These important features of the SHS technology often result in remarkably improved material properties in comparison with the same composites prepared by conventional ceramic techniques.

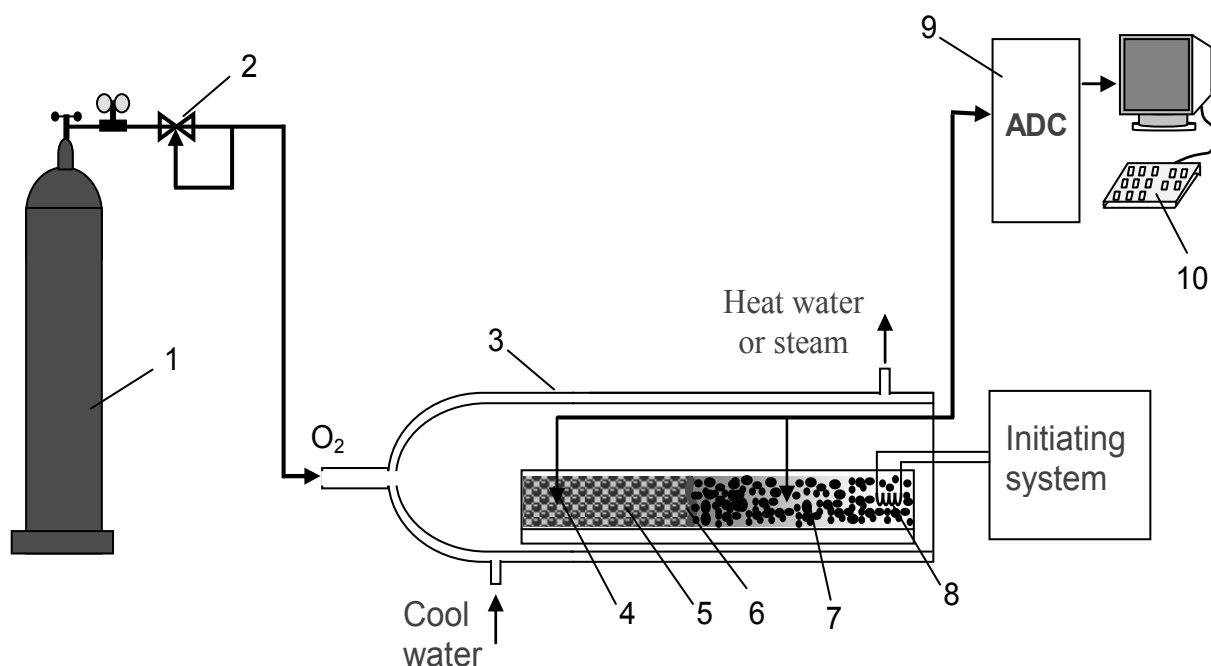


Fig. 1. Schematic of the technological equipment used for the SHS process. 1: oxygen; 2: oxygen flow controller; 3: quartz-tube reactor; 4: thermocouple; 5: green mixture; 6: combustion front; 7: end product; 8: igniter; 9: analog-digital convertor; 10: personal computer.

For the SHS experiments, the initial materials (Ti , TiO_2 , $SrCO_3$, and BaO_2) have been milled to powder with grain sizes of about 5-10 μm , dried, and thoroughly mixed. The mixture of reactant powders is then placed in a quartz-tube reactor and ignited by radiant energy from the heated wire. The use of oxygen as an oxidant and Ti as a fuel provides combustion temperatures of 1400-1800 $^{\circ}C$ and wave-front propagation velocities of 1-4 mm/s. To prepare targets for the PLD process, the synthesized SHS product has been milled to powders of 0.5-5 μm , pressed into pellets at a pressure of 4.5 ton/cm², and then heated at 1350 $^{\circ}C$ for 4-5 h.

3. Preparation of EFIS sensors and measurement set-up

In comparison to ferroelectric field-effect transistor structures, capacitive field-effect EFIS sensors are simple in layout and cost-effective in fabrication: usually, no photolithographic process steps or complicated encapsulation procedures are needed. The perovskite-oxide thin films (~100 nm thick) of $Ba_{0.25}Sr_{0.75}TiO_3$ and $Ba_{0.31}Sr_{0.69}TiO_3$ composition were prepared onto $Si-SiO_2$ substrates ($p-Si$, $\rho = 5-10 \Omega cm$; 50 nm SiO_2 , chip size: 10x10 mm²) by PLD technique using the targets fabricated by the SHS method. The main advantages of the PLD technique are its high flexibility, the compatibility with silicon planar technology, the controlled deposition of multi-component compositions as perovskite oxides in a defined stoichiometry as well as the short deposition time due to the high growth rates [18,19]. The BST films were deposited at 400 $^{\circ}C$ in an oxygen ambient (2×10^{-3} mbar) using a KrF excimer laser with a wavelength of 248 nm. The laser pulse length, frequency and energy were 20 ns, 10 Hz, and 2.5 J/cm², respectively. Before the PLD growth, a 300 nm thick Al film was deposited on the rear side of the chip as contact layer. For the details of the PLD process, see e.g., [19].

The prepared perovskite-oxide layers have been physically characterised (thickness, morphology, homogeneity, composition) by means of ellipsometry, scanning-electron microscopy (SEM), Rutherford backscattering spectrometry (RBS) and x-ray diffraction analysis (XRD) methods. As an example, Fig. 2 shows the cross-sectional SEM picture of a *BST-SiO₂-Si* layer structure. RBS measurements could verify the stoichiometric transfer from the original target material to the thin-film state. The amorphous structure of the films was controlled by additional RBS/channeling measurements and XRD measurements (not shown).

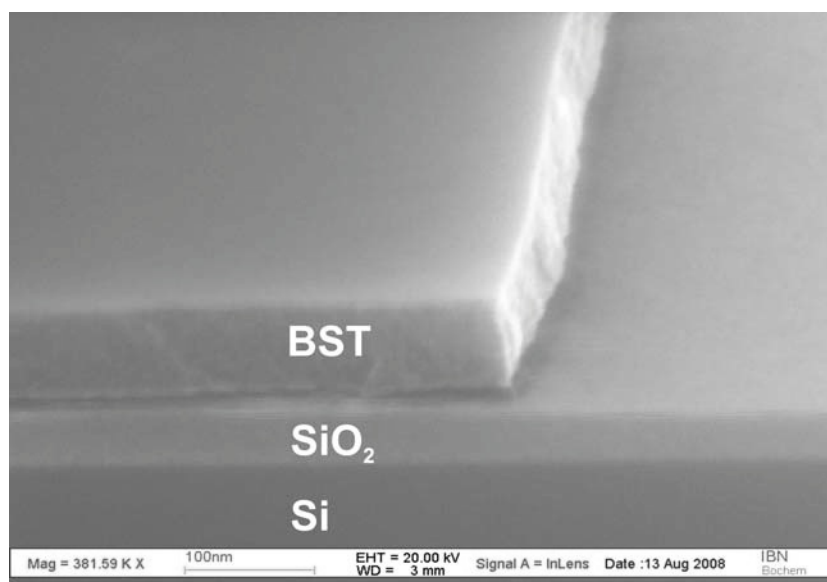


Fig. 2. SEM picture (cross-sectional view) of the *BST-SiO₂-Si* layer structure.

The pH-sensitive properties of the field-effect EFIS sensors were tested in buffer solutions from pH 3 to pH 11 by means of capacitance-voltage (C-V) and constant-capacitance (ConCap) methods using an impedance analyzer (Zahner Elektrik). The measurement set-up for the electrochemical characterisation of the EFIS sensors (left) and schematic of the layer structure (right) is presented in Fig. 3.

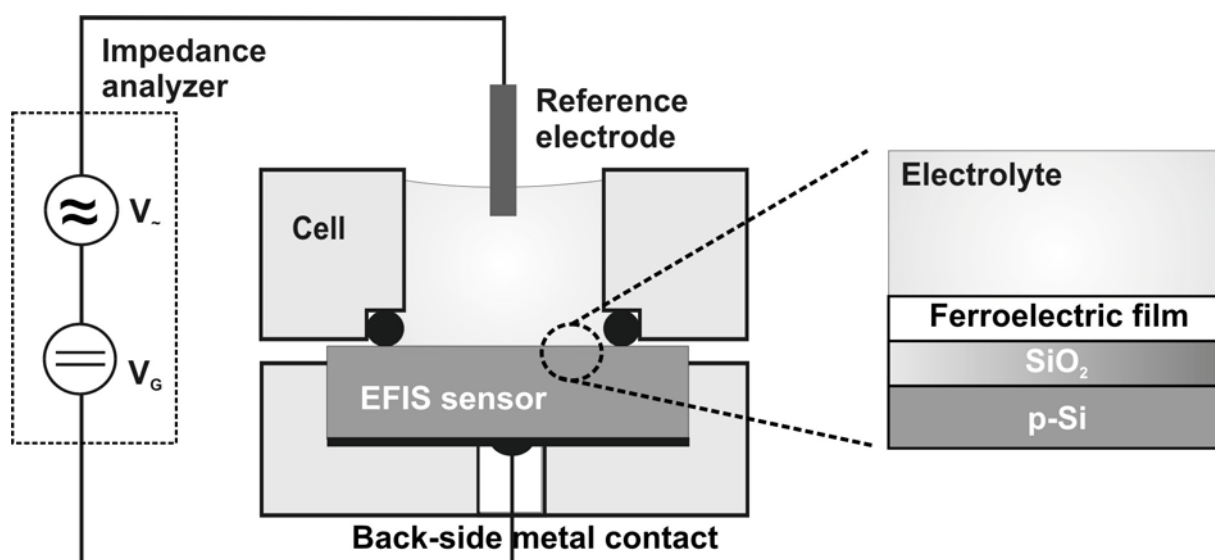


Fig. 3. Measurement set-up for the electrochemical characterisation of capacitive field-effect EFIS sensors (left), and schematic of the layer structure (right).

For the measurements, the EFIS sensor is mounted into a home-made measuring cell, sealed by an O-ring and contacted on its front side by the electrolyte and a reference electrode, and on its rear side by a gold-plated pin. A conventional liquid-junction $Ag/AgCl$ electrode is used as a reference electrode. For operating the EFIS sensor, a dc polarisation voltage is applied via the reference electrode to set the working point in the depletion range of the capacitance-voltage curve, and a small superimposed ac voltage with an amplitude of 20 mV is applied to measure the capacitance of the sensor. All potential values are referred to the $Ag/AgCl$ reference electrode. The side walls and backside contact of the EFIS sensor chip were protected from the electrolyte solution by means of an O-ring, thus avoiding the complicated encapsulation process. The contact area of the EFIS sensor with the solution was about 0.5 cm^2 . The measurements have been performed in a dark Faraday cage at room temperature.

4. pH sensitivity of EFIS sensor with BST films

Fig. 4a depicts a typical set of C-V curves for an EFIS sensor with a 100 nm thick $Ba_{0.31}Sr_{0.69}TiO_3$ layer measured in Titrisol buffer solutions with different pH values from pH 11 to pH 3. As expected, with decreasing pH, the C-V curves are shifted along the voltage axis in the direction of a more negative flat-band voltage due to the change of the additional potential drop at the electrolyte/BST interface. A similar behaviour has been observed for an EFIS sensor with a $Ba_{0.25}Sr_{0.75}TiO_3$ film as pH-sensitive gate material. The calibration curve of the sensor evaluated from the linear region of the C-V curves at ~60% of the maximum capacitance is shown in Fig. 4b. The EFIS sensors with both $Ba_{0.25}Sr_{0.75}TiO_3$ and $Ba_{0.31}Sr_{0.69}TiO_3$ films show an average pH sensitivity of 45-50 mV/pH. For some sensors, a pH sensitivity of 56-58 mV/pH has been observed that is comparable with pH-sensitivity values reported for Si_3N_4 (46-56 mV/pH), Al_2O_3 (49-57 mV/pH) and Ta_2O_5 films (55-59 mV/pH), which have often been utilised as pH-sensitive transducer material in ion-sensitive field-effect transistors [20-22]. The mechanism of the pH sensitivity of BST films can be explained by the protonation/deprotonation of the hydroxyl groups at the BST surface according to the site-binding model (see e.g., [20] and references there). The resulting pH-dependent electrical surface charge of BST leads to a modulation of the space-charge capacitance in the Si, thus generating a pH-dependent sensor signal that, in fact, was observed during the C-V measurements.

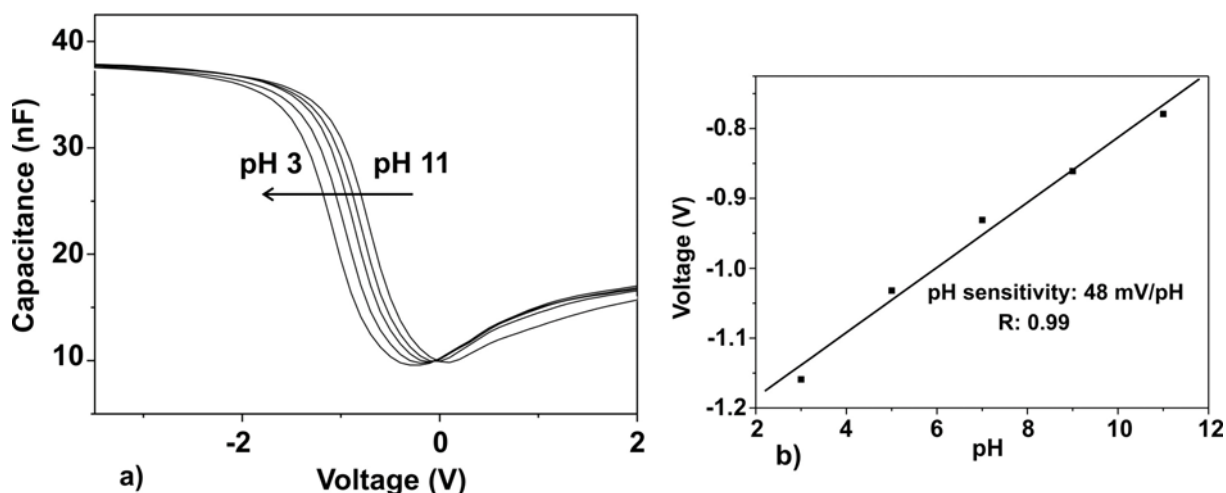


Fig. 4. Typical set of C-V curves (a) and calibration curve (b) for an EFIS sensor with a 100 nm thick $Ba_{0.31}Sr_{0.69}TiO_3$ layer measured in Titrisol buffer solutions with different pH values from pH 11 to pH 3.

Fig. 5 exemplarily demonstrates the dynamic pH response of an EFIS sensor with a $Ba_{0.31}Sr_{0.69}TiO_3$ layer recorded in different pH buffer solutions at a frequency of 100 Hz. In this experiment, the capacitance of the EFIS sensor has been kept at a fixed value within the depletion region of the C-V curve (a working point was chosen at ~60% of the maximum capacitance) using a feedback-control circuit, and the pH-dependent signal changes were directly recorded. As can be seen, the sensor signal shows a clear dependence on the pH value of the solution within the loop cycle of pH 7 → 3 → 11 → 3 → 7. The response time ($t_{90\%}$) was about 5-10 s.

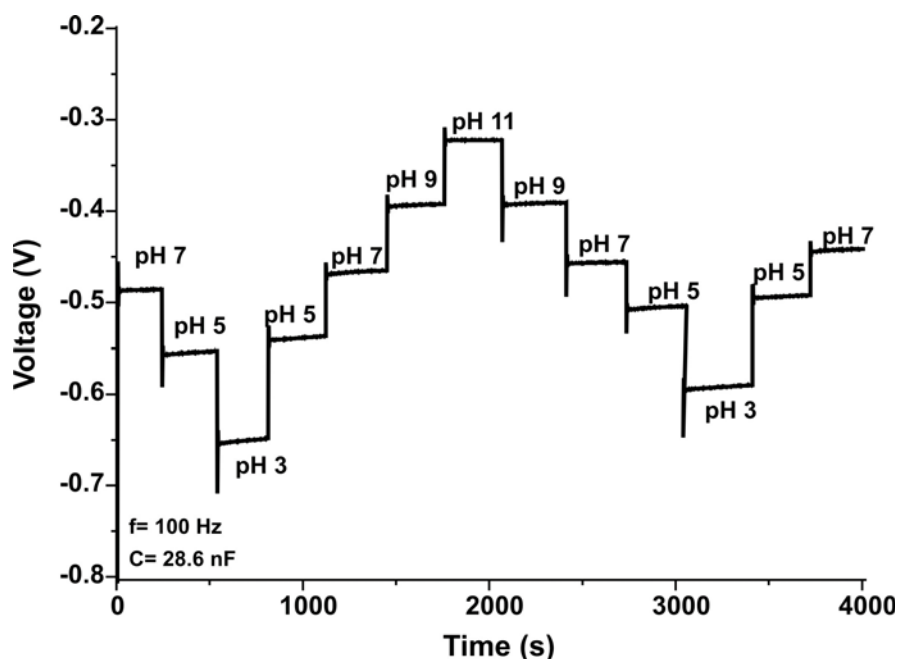


Fig. 5. ConCap response of an EFIS sensor with a $Ba_{0.31}Sr_{0.69}TiO_3$ film as pH-sensitive gate material in buffer solutions of different pH values.

5. Conclusions

The obtained results demonstrate the potential of PLD-prepared BST films as alternative gate material for capacitive field-effect pH sensors based on an electrolyte-insulator-semiconductor system. The main advantages of EFIS sensors are their simple structure, and the ecologically clean and cost-effective synthesis of the BST targets of desired composition and doping elements by means of the SHS technology. Future experiments will focus on a detailed investigation of the effects of composition (Ba content, doping, etc.), crystalline structure (amorphous, polycrystalline) and oxygen vacancies in the BST films on the sensitivity of the device. The hysteresis effects in EFIS sensors and the development of enzyme-modified field-effect EFIS sensors by using the high catalytic properties of BST films will be considered.

Acknowledgments

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