Sensorial properties of ferroelectric-semiconductor $(Ba_x Sr_{1-x}TiO_3 - p-Si)$ heterojunction

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Abstract. $p-Si/Ba_xSr_{1-x}TiO_3$ heterojunction sensorial properties in electrolyte solution are investigated. It is stated that the structure's capacitance and current exhibit certain sensitivity to pH of electrolyte medium. Based on experimental results we conclude that proposed heterojunction structures can be used as combined multifunctional sensor, where ferro-nanofilm can "work" in two directions: horizontal – as a gas, humidity and ion sensitive membrane and in vertical direction (with Si substrate) - as an ampereometric sensor and potentiometric field effect capacitance sensor.

Keywords: ferroelectric, heterojunction, pH-sensitivity

1. Introduction

The ferroelectric nanofilms and different structures based on them, which are quite compatible with the modern microelectronic technologies, during last years have shown their competitions in the fields of microwave active, passive elements application [1,2]. Because of the unique multifunctional material properties (ferroelectric, piezoelectric, microwave, electrooptic), the high permittivity (for example, $\varepsilon_{SrTiO_3} \approx 300$), very low dielectric losses, low leakage current, electric, pyroelectric, tunable features, good thermal and mechanical stabilities, perovskite type composite oxides of the ABO₃ system have received intensive research activities in many applications ranging from high-density dynamic random access memories (DRAM) and non-voltaic memory elements [3,4], voltage-tunable capacitors, ferroelectric field-effect transistors, over automotive and aerospace, communications and environmental monitoring [5,6] up to health care (ultrasonic medical imaging, thermal imaging systems, nondestructive evaluation, etc.), as well as gas, vapor, liquid biosensors [7,8].

During last decade, with the tremendous development of nanotechnologies, increasing attention was attributed to heterojunctions based on ferroelectric films grown on semiconductors (particularly $Ba_xSr_{1-x}TiO_3 - pSi, BST / Si$) [9-13]. These devices are a novel class of solid-state devices and are expected to be very promising for applications as information storage, surface acoustic wave resonators and tunable varactors, transducers and actuators (including ultrasonic, infrared and imaginary applications), micromechanical systems (MEMS), optoelectronics, and large potential for new multifunctional device applications. As a powerful rival of conventional Si-based structure, the ferroelectric-semiconductor heterostructures based devices have a great application potential in modern integrated ferroelectric-based memory devices too. Several studies on the atomic and electronic structure [9,12,13], band offsets [9,10], current transport behavior, rectifying [9], and photovoltaic [10,11] properties of ferroelectric-/semi-conductor (mainly with Si) heterojunctions have been reported. While their above-mentioned properties have been well studied, to our knowledge, very little is known so far about the ferroelectric/semiconductor heterojunction application for (bio-) chemical sensors.

In this connection, the goal of the article is to investigate some sensorial properties of ferroelectric/semiconductor ($Ba_xSr_{1-x}TiO_3 - pSi$) heterojunction in electrolyte solutions (Fig.1).

2. Results and discussions

The scientific and practice applied motivation (argumentation) of using the BST/Si heterojunction as a combined multifunctional sensor, according to our primary theoretical and experimental studies are the follow:

1) Taking into account the fact that almost all parameters of any heterojunction are in strong dependence on material, electrical, dielectric parameters, depletion layers characteristics, capacitances of heterojunction pairs, as well as in strong dependence on surface and interface conditions of heterojunction. To our opinion, the proposed structure in horizontal direction can be used as gas, humidity, ion and optically sensitive membrane, and in vertical direction (with Si) as an amperometric and the same time as potentiometric field effect capacitance sensor (Fig.1), which allowed to have multifunctional combined sensor structure, which, in turn, are very important for development of future "Lab-on chip" technology.

2) The magnitude of the leakage/injection current and the shape of the *I-V* curve of heterojunction depend on the conduction mechanisms, nature and density of the interface states, traps, etc. Moreover, it is well known and has been established in semiconductor and sensorial technique that the leakage/injection currents are an excellent "marker" and "tools" for characterization of processes that can take place in heterojunctions. Moreover, modern measure methods and systems allowed to measure current in the range of pico-amperes with very higher precisely and the measure procedures as well as measure equipment are simpler in compare with the measure of capacitances.



Fig. 1. The proposed Metal-Ba x Sr1-x TiO3-pSi-Al ferronanofilm structure and geometric sizes

By experimental and theoretical modeling and calculation of the heterojunction depletion layer width and capacitances it is established [14,15] that depending on Si-substrate impurity doping level as well as the presence in real conditions the higher concentration of oxygen vacancies (as an inevitable presented defects in ferroelectric materials) the depletion layer of heterojuction is mainly lied into Si-substrate. Thus, the heterojunction can be used as capacitive field-effect operated potentiometric sensor [7,8], where due to absorbed by ferrofilm different type of ions will be change of surface potential and thus to lead of corresponding change of the depletion layer capacitance of heterojunction.

From the other hand, the analyses of the BST/Si heterojunction current flow possible mechanisms it is shown [9,12,13], that the value of current is strongly depends on the built-in field and therefore depends on the surface potential. These dependences, in turn, means, that absorbed by ferrofilms different ions can leads to change of the barrier potential (height) of heterojunction and thus affect on value of heterojunction current, which we can use as a new sensor marker for ampereometric detection of concentration of absorbed ions.

In Fig. 2, Fig. 3 and Fig.4 are presented the results of experiments carried out for Al - p - Si - BST - Ag heterojunction structure's capacitance and current respectively, in different pH electrolyte solutions.



Fig. 2.The depletion layer capacitance dependence on voltage of Al-p-Si-Ba_{0.7}Sr_{0.3}TiO₃-Ag heterostructure for different values of electrolyte solution pH (f = 30 Hz, area of Ag contact - 0.042 cm² - 0.07 cm²)



Fig. 3. I-V characteristics of Al-p-Si-Ba_{0.7}Sr_{0.3}TiO₃-Ag heterojunction at different values of electrolyte's pH



Fig. 4. Current - pH dependence of Al-p-Si-Ba_{0.7}Sr_{0.3}TiO₃-Ag heterojunction (U= 3V, forward bias, other parametres from results of Fig.3)

3. Conclusions

As it follows from the figures, the $Al - p - Si - Ba_{0.7}Sr_{0.3}TiO_3 - Ag$ structure capacitance and current exhibits certain sensitivity to pH of electrolyte medium. However, for example, in the case of capacitance, it characterized very high hysteresis effects and for the current, it shows low sensitivity. Obtained results show that proposed heterojunction structures depending on principle of operation (sensitivity to change of current and capacitance) allow to use them as combined multifunctional sensor, where ferro-nanofilm can "work" in two directions: horizontal – as a gas, humidity and ion sensitive membrane, and in vertical direction (with Si substrate) - as an ampereometric sensor and potentiometric field effect capacitance sensor for evaluation and monitoring of liquid medium's biomedical parameters.

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