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ELECTRONIC PROPERTIES OF THIN NIOBIUM DOPED BARIUM TITANATE FILMS

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This work presents results of investigations of barium titanate thin films with Nb_2O_5 admixture, deposited on Si substrates by means of Radio Frequency Plasma Sputtering (RF PS) of sintered $BaTiO_3$ + Nb_2O_5 target. Round, aluminum (Al) electrodes were evaporated on the top of deposited layers. Thus, metal-insulator-semiconductor (MIS) structures were created with $BaTiO_3$ thin films playing the role of the insulator. They enabled subsequent electrical characterization (current-voltage (I-V) and capacitance--voltage (C-V) measurements) of studied material. This allowed extraction of several electronic parameters (e.g. ε_{ri}, ρ, V_{FB}, ΔV_H). Films composition were additionally studied using secondary ion mass spectroscopy (SIMS) techniques.

Key words: $BaTiO_3$, thin films
Słowa kluczowe: $BaTiO_3$, cienka warstwa

1. INTRODUCTION

Owing to advantageous electrophysical properties (in particular piezoelectricity, high dielectric constant and refractive index values), barium titanate $BaTiO_3$ (BT) ceramics have been one of the most extensively used dielectric materials in electronic applications like multilayer ceramic capacitors (MLCCs), surface acoustic wave (SAW) devices, microwave filters and resonators, optical waveguides, embedded

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capacitances in printed circuit boards, thermal imaging devices and actuators [1-7]. In these areas of applications $BaTiO_3$ has been used in a bulk or a thick layer form. More recently, barium titanate has been also attracting attention as a potential high-k dielectric for applications in dynamic access random memories (DRAM) [8-10] or non-volatile memories (NVM) [11], which however requires producing BT in a form of thin film.

For microelectronic applications such barium titanate films are usually obtained either in amorphous or polycrystalline form and posses worse parameters than the bulk or thick film material. However, for instance the dielectric constant value of thin film BT is typically still much higher than that of silicon dioxide.

There is variety of techniques that allow producing BT layers. Among the most commonly used are MOCVD, MBE, hydrothermal, sol-gel, RF sputtering and pulsed laser methods. This work presents results of investigations of $BaTiO_3$ thin films with Nb_2O_5 admixture, deposited on Si substrates by means of Radio Frequency Plasma Sputtering (RF PS) of sintered $BaTiO_3 + Nb_2O_5$ (2% wt.) target in argon plasma environment.

2. EXPERIMENTAL DETAILS

Approximately 100 nm thick barium titanite films were produced on p-type Si (<100>, ρ = 2-10 Ωcm) substrates using Radio Frequency Plasma Sputtering (RF PS) method. Schematic diagram of RF PS apparatus is shown in Fig. 1 while Tab. 1 presents parameters of the deposition process.

Round, aluminum (Al) electrodes were vacuum-evaporated on top of deposited layers. Thus, metal-insulator-semiconductor (MIS) structures were crated with BT thin films playing the role of the insulator. They enabled subsequent electrical characterization (current-voltage (I-V) and capacitance-voltage (C-V) measurements) of the studied material. Current-voltage characteristics were obtained using Keithley SMU 238 whereas high-frequency (10kHz-10MHz) C-V measurements were performed using HP 4061A test station.

Films chemical composition was investigated by secondary ion mass spectroscopy (SIMS) techniques.

Tab. 1. Parameters of the RF PS deposition process of $BaTiO_3$ thin films.
Tab. 1. Parametry procesu osadzania warstwy $BaTiO_3$.

Parameter	Value
Self-bias voltage [V]	280
Ar flow rate [ml/min]	10
Target–substrate spacing [mm]	15
Deposition time [min]	30

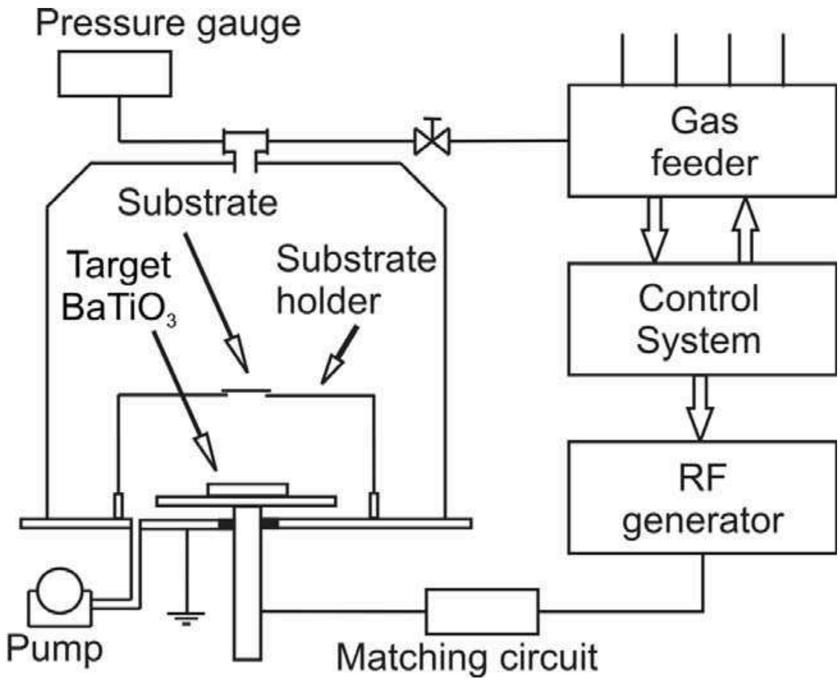

Fig. 1. Schematic diagram of the apparatus for radio frequency plasma sputtering (*RF PS*) deposition processes.
Fig. 1. Schemat urządzenia do wytwarzania warstw tytanianu baru metodą rozpylania w plazmie o częstotliwości radiowej.

3. RESULTS AND DISCUSSION

Fig. 2 present SIMS profile of investigated material. BT/Si interface region is sharp and narrow while the constant level of Ba, Ti and O signals suggest that the compound has a good stoichiometry. Produced films also contain undesired impurity (fluorine), which most likely originates from contaminated target or/and is an artifact of the Si substrate cleaning process.

As far as electrical measurements of fabricated MIS structures are concerned, first of all good reproducibility of observed I-V and C-V characteristics should be pointed out.

Typical I-V curves are presented in Figure 3, which demonstrates non-symmetrical character, Dielectric properties have lower values then was expected. Resistivity of studied material (@ ±10V) is of the order of 10^8 Ωcm. Breakdown measurements of dielectric strength of produced films reaching typically 1 $MVcm^{-1}$. All this parameters are quite low when we refer to [12].

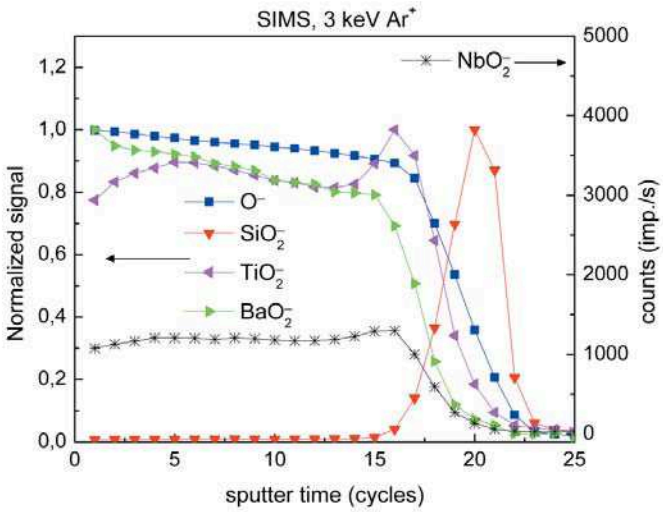

Fig. 2. SIMS profile of *RF PS* deposited BT film.
Fig. 2. Profil SIMS warstwy BT.

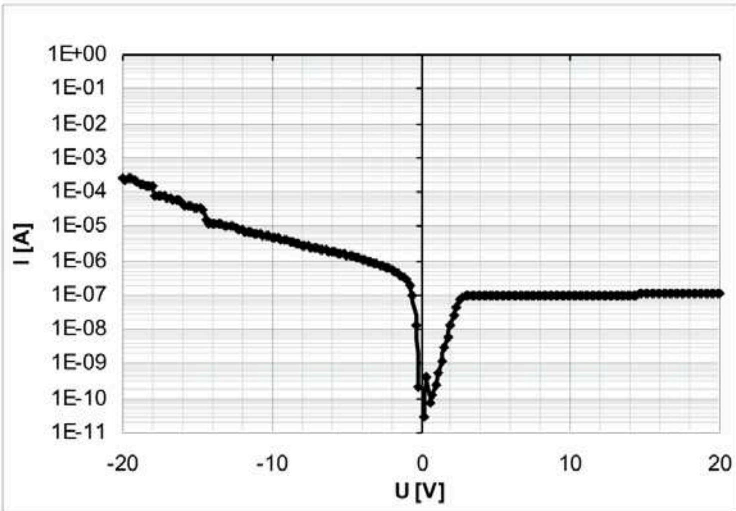

Fig. 3. Typical current voltage (*I-V*) characteristic of Al/BT/Si (*MIS*) structures.
Fig. 3. Typowe charakterystyki prądowo-napięciowe (*I-V*) struktur Al/BT/Si.

Fig. 4 shows in turn typical high-frequency C-V curves of investigated MIS structures. The origins of observed hysteresis in C-V characteristics (Fig. 4) can be established on the basis of their shape and direction [13]. Hysteresis caused by a drift of mobile ions in $BaTiO_3$ layers dominates in the test samples. This effect most likely might be attributed to the presence of impurities and nanograined structure of layers.

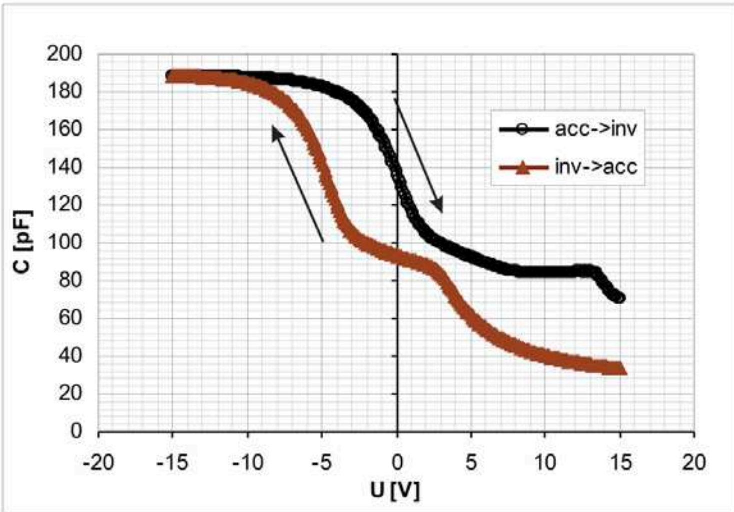

Fig. 4. Typical high-frequency capacitance-voltage (*C-V*) characteristics of Al/BT/Si (*MIS*) structures observed for the 1 MHz frequency value of the AC voltage component.
Fig. 4. Typowe wysokoczęstotliwościowe charakterystyki pojemnościowo-napięciowe (*C-V*) struktur Al/BT/Si zmierzone dla częstotliwości 1 MHz.

Hysteresis loop width ΔV_H have relatively high values (ΔV_H= 5V). C-V measurements also shown that relative dielectric constant ε_{ri} of the investigated BT films is approximately equal to 4, which is far lower than in the case of thick large-grained BT ceramics, and then we expected. Worth to notice is fact that flat band voltage is near zero.

4. CONCLUSIONS

In the course of RF PS process thin films of barium titanate were deposited on Si substrates. The obtained layers are dense and show smooth surface. However, large hysteresis loop and V_{FB} values observed in the course of measurements of produced MIS structures indicate that applied $BaTiO_3$ synthesis technique still requires optimization.

Dielectric constant value ε_{ri} was approximately equal to 4, but perhaps might be improved by applying some post-deposition procedures (e.g. using post-deposition annealing at the temperatures of at least 500ºC [14-15]). At this stage of proposed deposition technology development, fabricated layers demonstrate dielectric properties indicating that so produced thin film material after increasing of purity or annealing could be of potential interest as an alternative dielectric for certain microelectronic applications.

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SUMMARY

WŁAŚCIWOŚCI ELEKTRYCZNE CIENKICH WARSTW TYTANIANU BARU DOMIESZKOWANEGO NIOBEM

W pracy prezentowane są wyniki badań dotyczące cienkich warstw tytanianu baru ($BaTiO_3$) z domieszką Nb_2O_5. Powłoki zostały osadzone metodą rozpylania targetu w plazmie o częstotliwości radiowej (Radio Frequency Plasma Sputtering - RF PS), a następnie poprzez próżniowe naparowanie elektrod aluminiowych na powierzchnie $BaTiO_3$, zostały wytworzone struktury metal-dielektryk-półprzewodnik (MIS). Pozwoliło to na charakteryzacje elektryczną (pomiary prądowo-napięciowe (I-V) i pojemnościowo-napięciowe (C-V)) kondensatorów, gdzie warstwa tytanianu baru występowała jako dielektryk. Wyznaczone zostały parametry takie jak: ε_{ri}, ρ, V_{FB}, ΔV_H . Ponadto zmierzono profil warstwy przy użyciu spektroskopii mas jonów wtórnych (*secondary ion mass spectroscopy* - SIMS).