Proceedings

Study of Lead-Free Ferroelectric Composite Coatings by Impedance Spectroscopy †

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Abstract: The aim of the study is the preparation and electrical characterization of lead-free ferroelectric oxide $BaSrTiO_3$ in the composition with a piezoelectric polymer. The properties of the deposited films were compared with pristine oxide. Atomic force microscopy showed a smooth surface, and a regular and homogeneous distribution of particles of both components in the composite films. The dielectric properties (electric permittivity and dielectric loss) were investigated at different temperatures ranging from 5 to 130 °C. Impedance spectroscopy was applied in the frequency range 100–100 kHz. The dielectric constant increase with the addition of a piezoelectric polymer to the ceramic phase was demonstrated. It can be seen that the interface conditions at the electrodes are improved after inserting a piezoelectric polymer. The interpretation of the plots of the complex impedance vs. frequency, and the real part of the impedance vs. the imaginary part, give information about the polarization process revealed in the structures.

Keywords: ferroelectric composite; piezoelectric polymer; impedance spectroscopy; dielectric properties; polarization processes

1. Introduction

Recently, the microstructure and dielectric properties of the barium titanate based materials have been widely studied because of their importance in the lead-free feroelectric sensor technology [1]. Variety derivatives have been studied and different approaches, such as doping and nanostructuring have been applied to gain mostly the piezoelectric response in $BaTiO_3$ and $SrTiO_3$ based applications. The studies have revealed that the ferroelectric properties can be controlled by the deposition methods and the deposition conditions. To establish a relation between the microstructure and the ferroelectric response, a scanning electron microscopy (SEM), or atomic force microscopy (AFM), have been applied in combination with polarization P–E hysteresis curves [2]. However, information about some fundamental processes, such as dipole motions, which are responsible for the polarization processes, cannot be directly accessed from the SEM/AFM and P–E measurements. Therefore, a more sophisticated technique is necessary, such as impedance spectroscopy (IS). This relies on the bias signal supplied to the sample, which can vary in magnitude and frequency [3]. This technique could be applied at various temperatures over the samples [4]. Parameters like the full impedance and admittance, contact resistance, interface capacitance, dielectric permittivity, and loss tangent can be extracted from the impedance measurements. In addition, some major parameters of the ferroelectric structures, extracted from the IS, can be determined at different temperatures. All these parameters are important for the sensor technology, because they are related to the linearity of the response (contact resistance), time delay of the response (interface capacitances and their frequency dependence), thermal stability (dielectric permittivity and losses vs. temperature), impedance matching with the sensor signal's processing circuit (impedance/admittance of the sample), etc. It was found that the ferroelectric ceramic based structures, which are not fine granular, have exhibited a faster degradation of their electrical characteristics, which has been ascribed to the worsening of the contact properties between the grains (which are very often sharper depending on the materials' nature and crystallization degree) and the electrode films. Therefore, a buffer layer for interface smoothening is welcome. The poly (vinylidene fluoride-co-trifluoroethylene) fluoropolymer resin (PVDF-TrFE) is a suitable candidate for this purpose. In our previous study, we found that printed PVDF-TrFE on $BaSrTiO_3$ (BST) sputtered film exhibited an excellent performance, as well as that a composition between them arose due to the diffusion of the PVDF-TrFE particles between the crystallites of the BST [5]. This combination has been explored for energy harvesting and energy storage applications [6]. However, the effect of the composition PVDF-TrFE/BST on the ferroelectric sensors' contact resistance, interface capacitance, full impedance, and their frequency and temperature dependences has not been investigated yet. By the authors' knowledge, this is the first time the application of the impedance spectroscopy for the investigation of ferroelectric sensors on silicon with lead-free ceramic/polymer composite functional films has been performed.

2. Methods

Silicon wafers with orientation (100) were used as substrates. They were preliminary cleaned from the native SiO_2 by rinsing in 10% water solution of hydrofluoric acid, followed by a sonication bath in acetone. $BaSrTiO_3$ was radiofrequency RF sputtered on silver coated silicon wafers without additional oxidation of the target and without post-annealing of the films. The sputtering pressure was set to 2.5×10^{-2} Torr, and the sputtering voltage was 0.75 kV, defining a plasma power of 43 W/inch. The bottom and top electrodes were made of thermally evaporated silver films due to the great thermal and electrical conductivity of the silver. The top electrodes were patterned by a lift-off process to produce a variety of similar segments for impedance spectroscopy probing. The ferroelectric ink PVDF-TrFE was spin coated at 1000 rpm from Solvene 300 solution and then annealed at 120 °C in an oxygen atmosphere for 15 min to gain its ferroelectric phase. Atomic force microscopy was conducted by using the AFM model MFP-3D, Asylum Research, Oxford Instruments in non-contact mode for 2D and 3D imaging of the PVDF-TrFE coated and uncoated BST films' surfaces, Impedance spectroscopy was carried out by a chemical impedance analyzer IM3590 Hioki in the frequency range 100–100 kHz. The temperature measurements in the range 5–130 °C were realized by a home-made Peltier based heating–cooling system with smooth regulation of the temperature.

3. Results and Discussion

Figure 1 shows compared 2D and 3D AFM images of $BaSrTiO_3$ (left half of the images) and PVDF-TrFE coated BST (right half of the images). They reveal that large agglomerates in the range of 10 micrometer grains of perovskite phase were formed at BST sputtering on the silicon. On the top view it seems that a dense microstructure was formed; however, the tilted 3D image shows that there was a great variation in the BST film height at the interface area between the large crystallites (the height difference between the largest hill and hole was approximately 211 nm related to a total thickness of 480 nm). The spin-coating of the polymeric solution caused gaps filling and smoothening the BST film, as can be clearly seen from both images. A finer microstructure with an average roughness of less than 100 nm was observed for the smoother surface. It was expected that the improved film's flatness would result in a decrease in the losses and contact resistance due to the increased contact area at the interface's electrode/functional film.

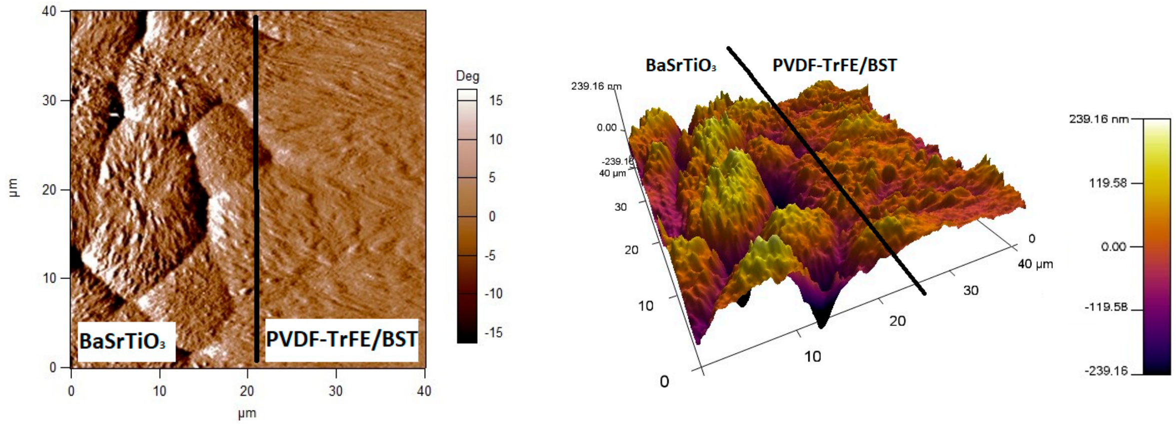

Figure 1. 2D and 3D atomic force microscopy (AFM) images comparing the surface topography of $BaSrTiO_3$ (BST) film and PVDF-TrFE coated BST film.

Dielectric constant, ε_r, and loss factor, D, were measured within the temperature range from 5to 130 °C (further temperature increase would change the crystal phase of the PVDF-TrFE polymer) at frequencies 100, 1, 10, and 100 kHz, for the pristine BST sample and PVDF-TrFE/BST. It was found that the dielectric permittivity was greater for the composite PVDF-TrFE/BST that was ascribed to interfacial polarization at the ceramic/polymer interface due to the difference of their conductivity and piezoelectric coefficients. It was also found that ε_r slightly decreased with the temperature for all set frequencies (Figure 2). Dielectric losses were found to be smaller for the PVDF-TrFE/BST, slightly dependent on the temperature, and more strongly dependent on the frequency (Figure 3). The results are in good agreement with the reported results for ferroelectric composites [7].

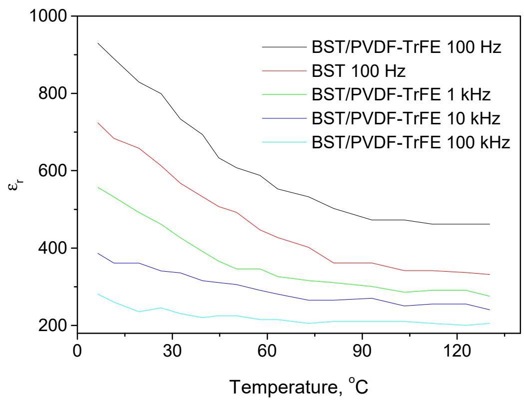

Figure 2. Variation of the permittivity with the temperature, frequency, and composition of the functional film.

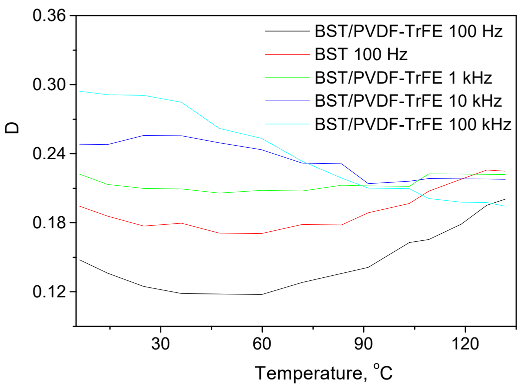

Figure 3. Variation of the loss factor with the temperature, frequency, and composition of the functional film.

4. Conclusions

AFM images show a smooth surface after the application of the PVDF-TrFE coating onto the BST surface and uniformly distributed peaks form the average roughness of the film. The structure with the composite film shows a high value of ε_r and a low loss factor, with poor temperature dependence, which is favorable for sensing applications relying on capacitor, or piezoelectric, principle. Future work will be related to full impedance measurements at different frequencies, analysis of the real and imaginary part behaviors, and the relation to the polarization processes in the ferroelectric film.

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