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Structural characterization and dielectric properties of $BaTiO_3$ thin films obtained by spin coating

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Abstract

Barium titanate thin films were prepared by spin coating deposition technique of an acetic precursor sol and sintered at 750, 900 and 1050 °C. Phase composition of the obtained thin films was characterized by X-ray diffraction and Raman spectroscopy. Their morphology was analysed by scanning electron microscopy and atomic force microscopy. Dielectric properties of thin films sintered at 750 and 900 °C were characterized by LCD device, where the influence of sintering temperature on dielectric permittivity and loss tangent was inspected. It was concluded that higher sintering temperature increases grain size and amount of tetragonal phase, hence higher relative permittivity was recorded. The almost constant relative permittivity in the measured frequency (800 Hz–0.5 MHz) and temperature (25–200 °C) ranges as well as low dielectric loss are very important for the application of $BaTiO_3$ films in microelectronic devices.

Keywords: *$BaTiO_3$, thin films, structural characterization, dielectric properties*

I. Introduction

In recent years performances and quality of microelectronic components have been extremely improved, and this rapid progress is the consequence of the fast development of new technologies and advanced materials. Nanostructured ceramic materials, especially thin films, take very important place in microchip industry. Barium titanate ($BaTiO_3$) is a well-known ceramic dielectric material that has the ability to be polarized, and store energy when exposed to external electric field. Very low dielectric loss and relatively high dielectric constant and polarizability are the main advantages of barium titanate materials [1,2]. Thanks to its dielectric properties, barium titanate is used for production of capacitors, and it is also a good candidate for application in ferroelectric memory. Tuning of dielectric properties can be achieved by addition of substituents at A or B positions in ABO_3 perovskite structure, but dielectric properties can also be modified by the microstructure control [1–5]. Different techniques can be used to obtain a desired structure and morphology of $BaTiO_3$, either by wet or vapour based deposition techniques. The vapour based deposition techniques require low pressures, high temperatures and complex instrumentation, but may provide films with better dielectric properties. On the other hand, the main advantages of wet-chemical techniques (such as spin coating) are that they are fast, cheap and do not require extreme conditions. In spin coating, a sol with small particle size gives the possibility to control film thickness and provides very fine film structure, but the choice of sintering procedure plays the essential role in obtaining dense structure without cracks and desired phase composition.

In this paper, $BaTiO_3$ thin films were obtained by spin coating of an acetic based sol on platinum coated silicon

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substrate and sintering at different temperatures. Since phase composition is closely related to processing conditions the inspection of the tetragonality trough X-ray diffraction and Raman spectroscopy, as a function of the sintering temperature, was used to analyse dielectric behaviour of the obtained $BaTiO_3$ thin films.

II. Experimental details

Thin barium titanate films were deposited on previously cleaned $Si/SiO_2/TiO_2/Pt$ substrate by spin coating deposition technique. For the preparation of $BaTiO_3$ sol, $BaCO_3$ and titanium butoxide were used as precursors and glacial acetic acid as a solvent. The concentration of the precursor sol was 0.25 M, with viscosity of around 5 mPa/s, and particle size around 2 nm in diameter [6]. In total, six layers of $BaTiO_3$ were deposited on the substrate at 3000 rpm for 30 seconds, where each layer was calcined at 500 °C for 5 minutes in order to evaporate all traces of solvent and partially consolidate the system. From the previous research [7], it was concluded that formation of barium titanate crystal phase forms on temperatures above 600 °C and 900 °C is the lowest sintering temperature at which a considerable amount of tetragonal phase can be formed. Due to mentioned reasons, the as-prepared $BaTiO_3$ films were sintered at 750, 900 and 1050 °C for 30 minutes.

X-ray diffraction patterns were recorded by Rigaku, MiniFlex 600 instrument, using Ni-filtered CuKα radiation. The data were collected over 2θ range 20–60° with a step size 0.03° and a speed of 3 s/step. Raman spectra were obtained by using Thermo Scientific DXR Raman Microscope, equipped with green laser (wavelength 532 nm). Morphology and layer structure of films were investigated with SEM (JEOL, JSM 6460LV) operating at 20 kV. The surface morphology was investigated by atomic force microscopy, AFM (DI CPII, Veeco). Dielectric measurements were performed on LCR device (GW INSTEK LCR-8101) in the frequency range 800 Hz–0.5 MHz and range of temperatures up to 200 °C. Top electrode was made of sputtered gold, with thickness of around 40 nm. Micropositioning probes (Signatone S-725) were used to establish a contact with the top (gold) and bottom (platinum) electrodes.

III. Results and discussion

3.1. Structural characterization

X-ray diffraction patterns of $BaTiO_3$ thin films deposited on $Si/SiO_2/TiO_2/Pt$ substrate, sintered on 750 and 900 °C for 30 min are presented in Fig. 1. It can be observed that all reflections can be assigned to perovskite phase or platinum [8]. The increase in sintering temperature causes $BaTiO_3$ diffraction picks to become more narrow and intense, as a consequence of grain growth. Obtaining the desired grain size is essential for good ferroelectric properties, while too small $BaTiO_3$ grains can limit the formation of tetragonal phase [9,10]. It is important to mention that there is no characteristic splitting of the pick at 2θ ~45° for tetragonal phase in $BaTiO_3$ films sintered at 750 and 900 °C (Fig. 1), but as the XRD pick is relatively broad it is difficult to distinguish whether the films have cubic structure or contain some amount of tetragonal phase. It is well-known that identification of characteristic pick spit at 2θ ~45° for tetragonal $BaTiO_3$ phase can pose a problem, especially with thin films obtained by sol gel technique. The characteristic peak splitting is obvious only for the film sintered at 1050 °C (Fig. 2). Crystal plane (200) in cubic $BaTiO_3$ that corresponds to diffraction pick at ~45° contains one central Ti^{4+} atom. Since cubic crystal unit is characterized by complete symmetry ($a = b = c$ and $\alpha = \beta = \gamma = 90°$) all Ti^{4+} ions are located exactly in the centre of crystal unit cell. Tetragonal crystal unit cell is also characterized by the identical angles which are 90°, but c parameter is distorted along z axes, and slightly longer than a and b unit cell parameters. This gives an opportunity to Ti^{4+} ion to locate itself along the z axes and create crystal planes on close distance (200) and (002), slightly misplace from cubic (200) crystal plane

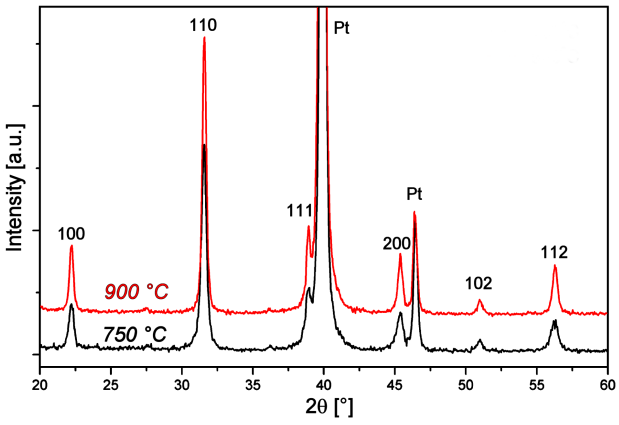


Figure 1. X-ray diffractograms of $BaTiO_3$ films on platinum substrate sintered at 750 and 900 °C (insert XRD of $BaTiO_3$ film sintered at 1050 °C)

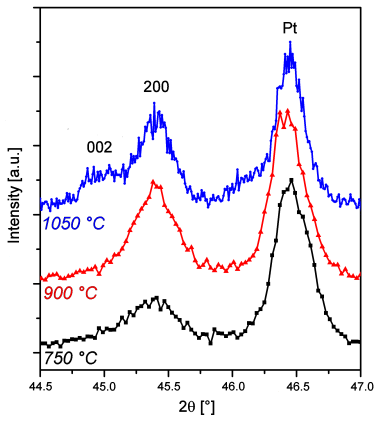


Figure 2. XRD patterns of $BaTiO_3$ films on platinum substrate sintered at 750, 900 and 1050 °C (for the selected 2θ range from 44.5 to 47.0)

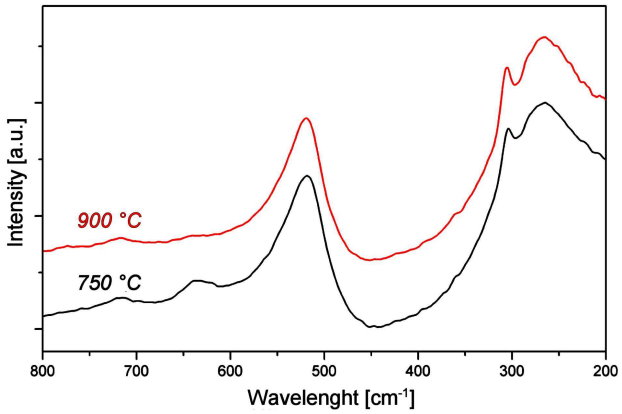


Figure 3. Raman spectras of $BaTiO_3$ deposited on platinum sintered at 750 and 900 °C

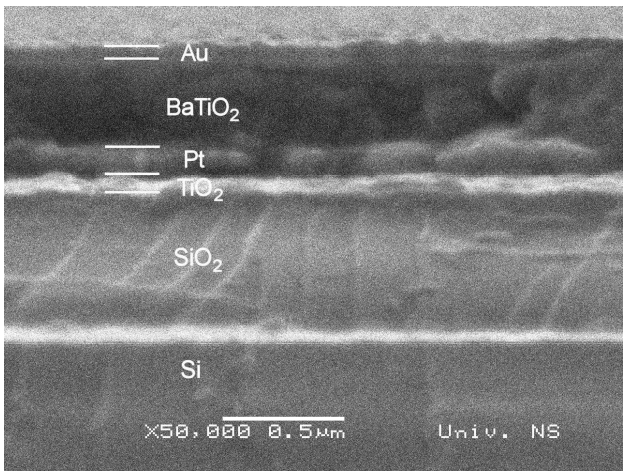


Figure 4. SEM micrograph of $BaTiO_3$ film deposited at $Si/SiO_2/TiO_2/Pt$ substrate and sintered at 900 °C for 30 minutes

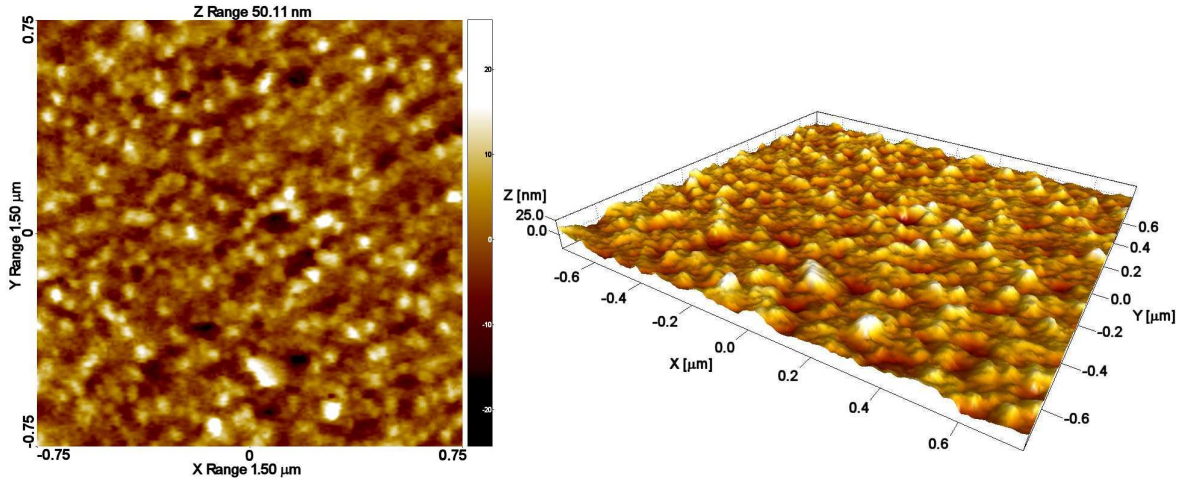
position. However, identifying those planes in $BaTiO_3$ thin films requires powerful X-ray diffraction device.

Raman spectroscopy is complementary to XRD characterization. While X-ray powder diffraction could be used to establish an average symmetry (long-range ordering), Raman scattering provide information about the local symmetry (short-range ordering) of materials. In theory, cubic $BaTiO_3$ phase has no Raman active modes, but tetragonal phase has a number of optically active modes all of which are Raman active. Specifically, optically silent F_{1u} modes in paraelectric phase splits into doubly degenerate E mode and a nondegenerate A_1 mode, and the F_{2u} mode splits into E and B_1 modes in tetragonal phase [9,11]. This provides an opportunity to identify ferroelectric barium titanate crystal phase in samples with low tetragonality ratio. The Raman response of the obtained thin films is obvious, since characteristic bands of barium titanate are clearly seen in Fig. 3. Broad peak at 720 cm^{-1} corresponds to vibration of $E(LO)$ mode of tetragonal phase, and at around 640 cm^{-1} can be observed broad band characteristic for hexagonal $BaTiO_3$ [12]. The intensity and sharpness of bands at 306 cm^{-1} and 520 cm^{-1}, which can be assigned to E and $E(TO)$ modes, respectively, are characteristic for tetragonal phase, and can be used to determine the c/a ratio [9,11]. Those results confirm that both $BaTiO_3$ films (sintered at 750 and 900 °C) contain in addition to cubic some amount of tetragonal perovskite phase. It seems that, at higher temperature (900 °C), the peak characteristic for hexagonal phase at 640 cm^{-1} disappears and some of the picks characteristic for tetragonal phase are more pronounced (such as the one at 306 cm^{-1}). Since, Raman spectroscopy reveals local lattice distortions in barium titanate crystal structure, the results of Raman spectroscopy indicate the presence of lower-symmetry crystal structures (tetragonal) despite the fact the cubic symmetry was determined by XRD. This disagreement could be explained by the fact that XRD deals with average and static symmetry, while Raman scattering refers to local and dynamic symmetry. Thus, Raman analysis, together with XRD results, indicates that the film sintered at 900 °C has somewhat coarser grain structure, contains higher amount of tetragonal $BaTiO_3$ phase and therefore higher dielectric constant is likely to be expected [12]. It is important to add that the tetragonal $BaTiO_3$ structure is confirmed by XRD only in the film sintered at 1050 °C (Fig. 2).

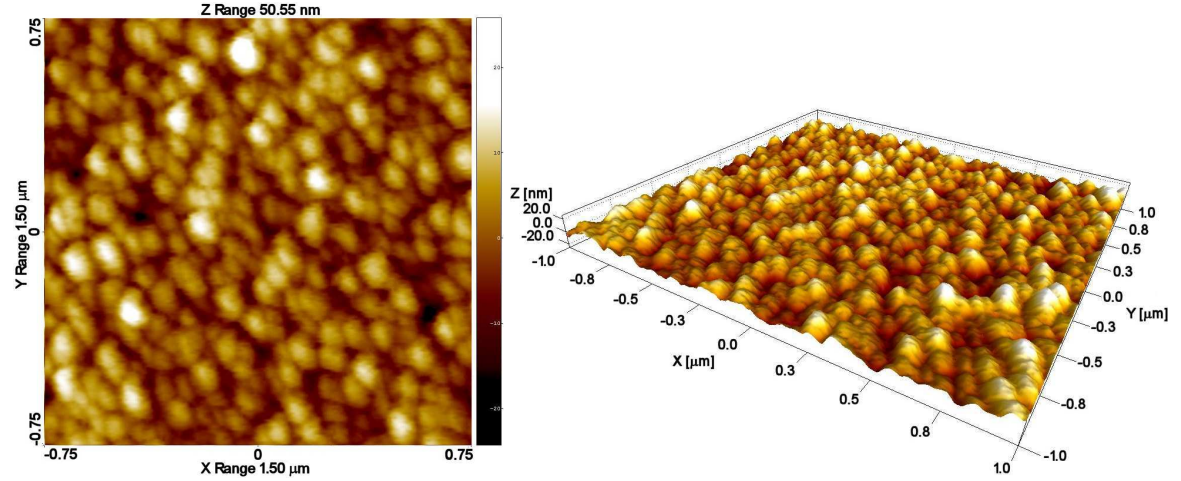
Figure 4 represents SEM micrograph of $BaTiO_3$ films on $Si/SiO_2/TiO_2/Pt$ substrate. It can be seen that films have uniform thickness of around 300 nm, with crack free dense structure, and good adherence to the substrate. In addition, different substrate layers, Si, SiO_2, TiO_2 and Pt, can be clearly seen (Fig. 4). Atomic force microscopy (Fig. 5) confirms the presence of flat surface and dense structure, and round shaped grains on nanometer scale. It is notable that grain size has increased on higher sintering temperature from ~25 nm at 750 °C, ~40 nm at 900 °C to ~90 nm at 1050 °C.

3.2. *Dielectric measurements*

Dielectric constant has been calculated using standard equation for parallel plate capacitor $\varepsilon_r = C \cdot d/(A \cdot \varepsilon_\circ)$, where C is the measured capacitance, d is thickness of film, A is overlapping area of the capacitor plates and $\varepsilon_\circ$ stands for permittivity of the vacuum. Figures 6 and 7 represent frequency-dependent relative permittivity (in range from 800 Hz to 0.5 MHz) at room temperature and temperature-dependent relative permittivity at frequencies of 1, 10 and 100 kHz, respectively. It can be observed that relative permittivity of ε_r ~200 characterizes the film sintered at 750 °C and is almost independent of frequency and temperature over the measured ranges. As expected, the sample sintered at 900 °C, characterized by higher tetragonal distortion, has three times higher value of dielectric constant (i.e. ε_r ~600 was measured). In addition, a slight change of ε_r with frequency and temperature can also by noticed. Similar results are obtained by Liu *et al.* [13] and Xu *et al.* [14] for chemical solution deposited $BaTiO_3$ films. The variation of dielectric loss as a function of temperature for the films sintered at 750 and 900 °C are shown in Fig. 8.



(a)



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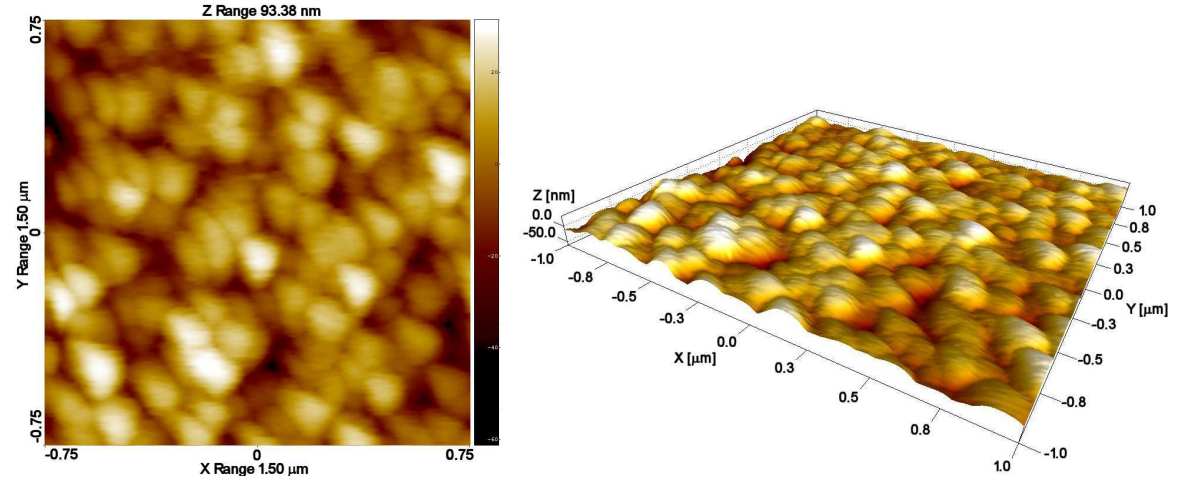

(c)

Figure 5. AFM analysis of $BaTiO_3$ films sintered for 30 minutes at: a) 750, b) 900 and c) 1050 °C

Very small values of loss tangent are measured for both films, with somewhat higher values for the $BaTiO_3$ film sintered at 900 °C. The constant relative permittivity in the measured frequency and temperature ranges as well as low dielectric loss are very important for the application of $BaTiO_3$ films in microelectronic devices [1,2].

IV. Conclusions

Thin barium titanate films were successfully obtained by spin coating deposition technique. According to XRD results it was difficult to distinguish whether the films sintered at 750 and 900 °C have cubic struc-

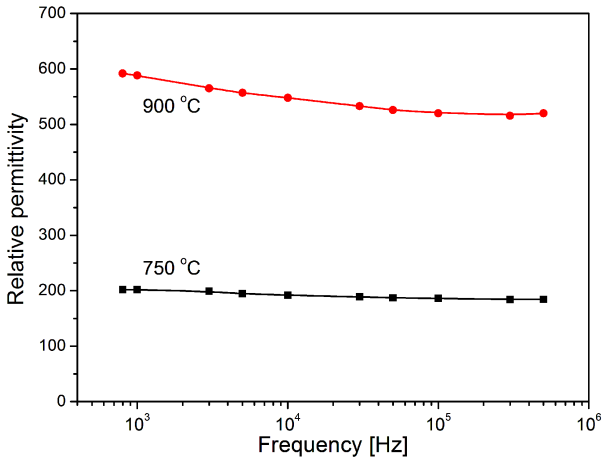

Figure 6. Frequency dependence of relative permittivity of $BaTiO_3$ films (sintered at 750 and 900 °C) at room temperature

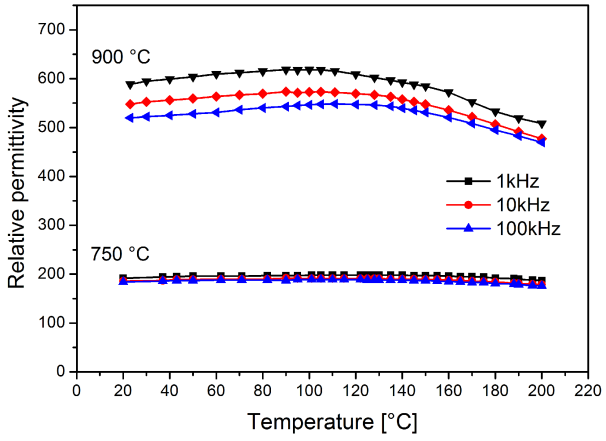

Figure 7. Temperature dependence of relative permittivity of $BaTiO_3$ films (sintered at 750 and 900 °C) at 1, 10 and 100 kHz

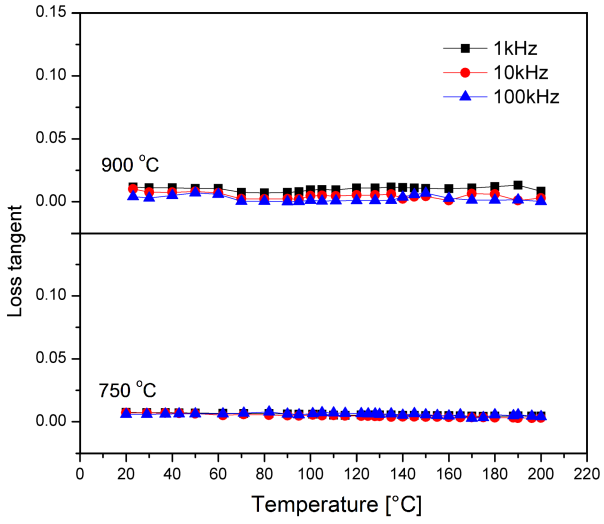

Figure 8. Temperature dependence of loss tangent of $BaTiO_3$ films (sintered at 750 and 900 °C) at 1, 10 and 100 kHz

ture or contain some amount of tetragonal phase. The tetragonal $BaTiO_3$ structure was observed by XRD only in the film sintered at 1050 °C. The increase of the grain size was recorded by X-ray diffraction analysis and atomic force microscopy, where diameter of round shaped grains increases with temperature from ~25 nm at 750 °C, ~40 nm at 900 °C to ~90 nm at 1050 °C. Sintered films were 300 nm thick, characterized by dense and crack free structure, and good adherence to the substrate. Raman spectroscopy compliments X-ray diffraction patterns and confirms the increase in c/a ration on higher temperatures, since crucial peaks for tetragonal phase in Raman spectra have become more emphasized in the sample sintered at 900 °C for 30 minutes. Dielectric constant of ε_r ~200 characterizes the film sintered at 750 °C and is almost independent of frequency and temperature over the measured range, whereas three times higher value (i.e. ε_r ~600) was obtained for the film sintered at 900 °C. Very small values of loss tangent are measured for both films, with somewhat higher value for the $BaTiO_3$ film sintered at 900 °C.

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