

Dielectric enhancement of sol–gel derived BaTiO₃/SrTiO₃ multilayered thin films

Run Xu^a, Mingrong Shen^{a,*}, Shuibing Ge^a, Zhaoqiang Gan^a, Wenwu Cao^b

^aDepartment of Physics, Suzhou University, Suzhou 215006, PR China

^bMaterials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

Received 1 August 2001; received in revised form 7 January 2002; accepted 7 January 2002

Abstract

Polycrystalline BaTiO₃/SrTiO₃ multilayered thin films have been prepared on Pt/Ti/SiO₂/Si substrates by a sol–gel processing. The X-ray diffraction (XRD) patterns and Auger electron spectroscopy (AES) indicate that the multilayered thin films were formed. The dielectric constant of the multilayered films was significantly enhanced and the dielectric loss was almost the same as that of the uniform BaTiO₃ and SrTiO₃ thin films. A dielectric constant of 660 at 1 kHz was observed for a stacking periodicity of 66 nm at room temperature and the corresponding dielectric loss was maintained below 0.05. The study indicates that there are some differences between the multilayered films and the uniform films in the dielectric constant–frequency relation and capacitance–voltage characteristics. The report also analyzes the mechanism of dielectric enhancement of the multilayered thin films prepared by the sol–gel process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dielectric properties; Multilayered thin films; Sol-gel processing

1. Introduction

Thin films of high dielectric constant materials such as BaTiO₃, SrTiO₃ and Ba_{1-x}Sr_xTiO₃ (BST) have drawn great attention over the last few years for the application of these materials in dynamic random access memories (DRAMs) [1–3]. Several generic methods have been considered to enhance the capacitance per area, such as doping, changing electrode material, ferroelectric superlattices and multilayered thin film [4–12]. Recently, significant experimental efforts have been devoted to the fabrication of ferroelectric superlattices. Typically, Tabata et al. observed an enhancement of dielectric constant from 500 to 900 at 10 kHz in the epitaxial superlattices of BaTiO₃/SrTiO₃ for a stacking periodicity of approximately 8 Å at room temperature [4]. Erbil et al. [5] observed extremely high dielectric constants of 420 000 at 1 kHz and at room temperature in epitaxial PbTiO₃/Pb_{0.72}La_{0.28}TiO₃ heterostructures for a stacking periodicity of 40 nm. Qu et al. [6] reported the relaxational behavior in polycrystalline BaTiO₃/SrTiO₃ mul-

tilayered thin films deposited on Pt/Si substrates with periodicities from 1.6 to 40 nm, but no obvious dielectric enhancement was observed in such multilayer structures.

Recently, Gregg et al. [7,8] reported the dielectric enhancement in epitaxial Ba_{0.8}Sr_{0.2}TiO₃/Ba_{0.2}Sr_{0.8}TiO₃ superlattice for the stacking periodicity less than 10 nm and found this phenomenon is associated with the onset of Maxwell–Wagner (MW) behavior. They also pointed out that the whole superlattice can be considered to be composed of two different kinds of dielectric layers. One is the interface-like layer of high conductivity, the other is the bulk-like layer of low conductivity, so the experimental results can be explained using the MW capacitance model. Their study suggests that the dielectric enhancement may also appear in other dielectric multilayered thin films system as long as a low-resistivity interfacial region is formed between bulk-like insulating dielectrics. However, till now, the dielectric enhancement in multilayered thin films is mostly observed in epitaxial thin films prepared on oxide substrates, and is generally associated with high dielectric loss. To our knowledge there is no observation on the dielectric enhancement in polycrystalline multilay-

*Corresponding author.

E-mail address: mrshen@suda.edu.cn (M. Shen).

ered thin films deposited on Si substrates, which are more compatible with large-scale integration than oxide substrates. In this paper, we report on the dielectric enhancement in polycrystalline BaTiO₃/SrTiO₃ multilayered thin films prepared on Pt/Ti/SiO₂/Si substrates by sol–gel processing.

2. Experimental details

To produce the multilayered BaTiO₃/SrTiO₃ films, two solutions were prepared for deposition by spin-coating. The raw materials for the solution synthesis were barium acetate [Ba(CH₃COO)₂], strontium acetate [Sr(CH₃COO)₂], and titanium butoxide [Ti(OC₄H₉–*n*)₄]. Glacial acetic acid (CH₃COOH) and methanol (CH₃OH) may be a stabilizer and solvent, respectively. Barium acetate or strontium acetate was dissolved into heated acetic acid. The solutions were then mixed and stirred. The equimolar amounts of titanium butoxide were added into the mixture and then the mixture was stabilized by appropriate methanol. The clear yellowish solution was finally prepared. The solutions in sealed bottles are stable and no crystallite forms for several months. The concentration of the final solution can be adjusted to 0.2 mol/l by adding appropriate quantity of solvent. The whole process of the preparation of the precursor solution was prepared in an ambient atmosphere.

Spin-coating was employed to deposit the filtered solution (syringe filters with 0.1 μm pore diameter) at 4500 rpm for 40 s onto the Pt/Ti/SiO₂/Si substrates. The wet films were pyrolyzed at 120 °C for 2 min just after deposition and then annealed at 750 °C for 8 min. The films were obtained by multiple repetitions of the deposition. In this work, all the films were 396 ± 6 nm thick, with a deposition of 12 layers. We prepared two multilayered thin films with different periodicity. The periodicity of sample A is 66 nm, which indicates the thickness of each BaTiO₃ layer or SrTiO₃ layer is 33 nm. The periodicity of sample B is 132 nm, and the thickness of each BaTiO₃ layer or each SrTiO₃ layer is 66 nm. The bottom layer of all the multilayered films is BaTiO₃ and the top layer is SrTiO₃. As references, the uniform films of BaTiO₃ and SrTiO₃ with same thickness were also prepared under the same conditions. It can be noted that all the films experience the same total time for heat treatment at a temperature of 750 °C.

The structure of the film was analyzed by a Rigaku D/MAX 3C XRD diffractometer using CuKα radiation at 40 KV. The microstructure of the film was investigated using a Hitachi S-5750 SEM. The electric measurements were performed on the films in metal–insulate–metal (MIM) configuration. Pt dots of 0.25 mm in diameter were prepared by RF-sputtering through a mask on the films to form MIM capacitors. The dielectric constant and loss measurements were

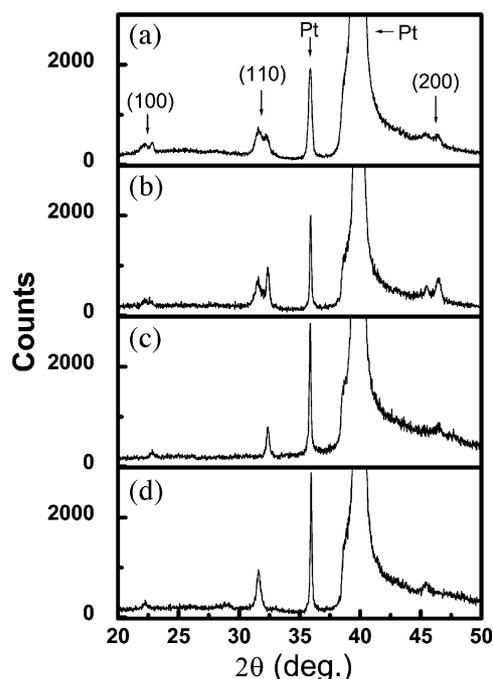


Fig. 1. The XRD patterns of (a) BaTiO₃ (33 nm)/SrTiO₃ (33 nm), (b) BaTiO₃ (66 nm)/SrTiO₃ (66 nm), (c) SrTiO₃ and (d) BaTiO₃.

carried out with a HP4192A LF impedance analyzer. The film thickness was determined with an ET350 Talysurf profilometer (Kosaka Laboratory Ltd.) after selective etching in buffered HF.

3. Results and discussion

Fig. 1 shows the XRD patterns of BaTiO₃/SrTiO₃ multilayered thin films. There are many peaks on each pattern, which indicates that these samples were polycrystalline in nature with a perovskite structure. No minority phase such as BaCO₃, SrCO₃ and TiO₂ was observed. The XRD patterns are composed of two sets, one for BaTiO₃, the other for SrTiO₃, as is shown in the XRD patterns of multilayered thin films (Fig. 1a for the stacking periodicity of 66 nm and Fig. 1b for 132 nm). The result indicates that the phase of BaTiO₃ and SrTiO₃ were not diffused together and did not form the solid solution under the conditions that each layer annealed at 750 °C for 8 min, but formed the multilayered structure.

Fig. 2 shows the composition depth profile of a typical BaTiO₃ (66 nm)/SrTiO₃ (66 nm) film determined by using a combination of AES and Ar ion etching. The results confirm that the concentration of Ba and Sr periodically fluctuate with the thickness, and the molar ratio of (Ba + Sr)/Ti/O is approximately 1:1:3 at any depth. The depth profile also indicates that there is an apparent interface layer between the BaTiO₃ and SrTiO₃ layers.

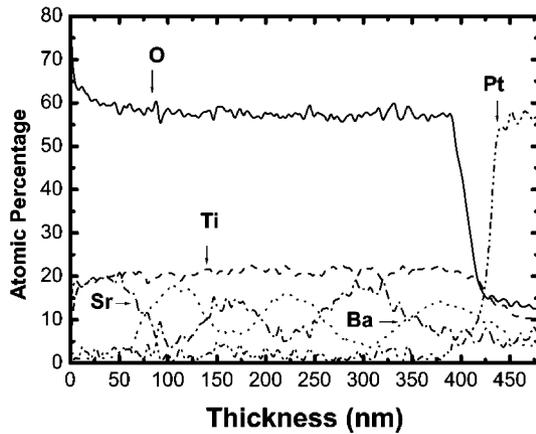


Fig. 2. Auger depth profile showing thickness distribution of compositions of a typical BaTiO₃ (66 nm)/SrTiO₃ (66 nm) film.

The SEM micrographs as shown in Fig. 3, show the films to be crack-free, and of uniform size grains. The grain sizes were estimated from the SEM micrographs using the intercept method, and the grain sizes of multilayered thin films A and B were approximately 40 nm, and almost the same as that of the uniform SrTiO₃ thin film due to the SrTiO₃ layer as the top layer. While the grain size of the uniform BaTiO₃ thin film was approximately 60 nm.

Fig. 4 shows the dielectric constant as a function of frequency at room temperature. It can be observed that the dielectric constants of multilayered thin films were larger than that of uniform thin films. At a frequency of 1 kHz, the dielectric constant of BaTiO₃, SrTiO₃, BaTiO₃ (33 nm)/SrTiO₃ (33 nm), and BaTiO₃ (66 nm)/SrTiO₃ (66 nm) was 348, 270, 422 and 660, respectively. The dielectric constant of the uniform BaTiO₃ and SrTiO₃ thin films is comparable with that reported by others [13] for films deposited by the sol-gel process. We also checked the dielectric constant of the uniform Ba_{0.5}Sr_{0.5}TiO₃ thin films by the same sol-gel process and found that it is also below 400 in the frequency range of 100 Hz to 1 MHz. From Fig. 4, it can be noted that the dielectric constants of all the examples decrease as the frequency increase, and the frequency dispersion of the multilayered thin films were different from that of the uniform films. In the frequency range of below 10⁹ Hz, the dielectric constant of the condensed matter as a function of frequency complies with the following relation [14]:

$$\epsilon = a + bf^{n-1}$$

where the parameters a and b are associated with temperature, and n is the dispersion parameter, $0 < n < 1$. We set the values of n to be 0.961, 0.961, 0.854 and 0.854 in BaTiO₃, SrTiO₃, BaTiO₃ (33 nm)/SrTiO₃ (33 nm) and BaTiO₃ (66 nm)/SrTiO₃ (66 nm), respectively, and set the appropriate values of a and b to plot a fitting

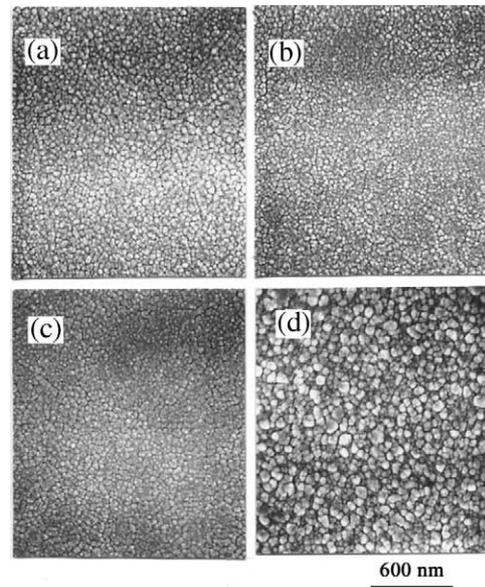


Fig. 3. The SEM surface micrographs of (a) BaTiO₃ (33 nm)/SrTiO₃ (33 nm), (b) BaTiO₃ (66 nm)/SrTiO₃ (66 nm), (c) SrTiO₃ and (d) BaTiO₃.

curve at the same time. As shown in Fig. 4, the result agrees well with the experiment. Obviously, the frequency dispersion of the multilayered thin films was larger than that of the uniform thin films.

A dielectric constant of 527 at 100 kHz was reported recently in SrTiO₃/BaTiO₃ multilayered thin films [15], and explained as the sum of each individual thin films using a series connection model. However, in our experiment, the dielectric constants of all the uniform thin films, including SrTiO₃, BaTiO₃ and Ba_{0.5}Sr_{0.5}TiO₃ films are less than those of the multilayered films. In addition, we measured the film thickness several times and found all the films were approximately 396 ± 6 nm in thickness. And all the films showed random crystalline orientation under present preparation conditions from

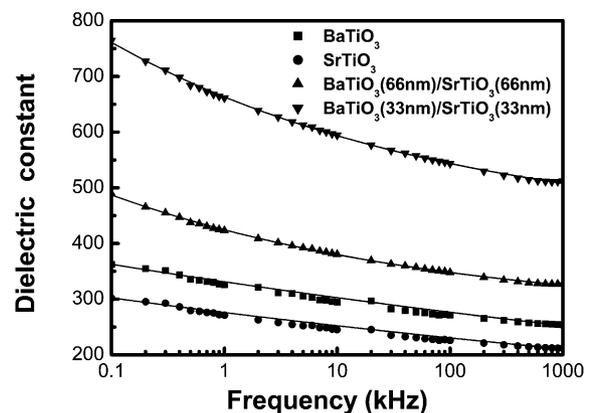


Fig. 4. The frequency dependence of the dielectric constant of all films at room temperature.

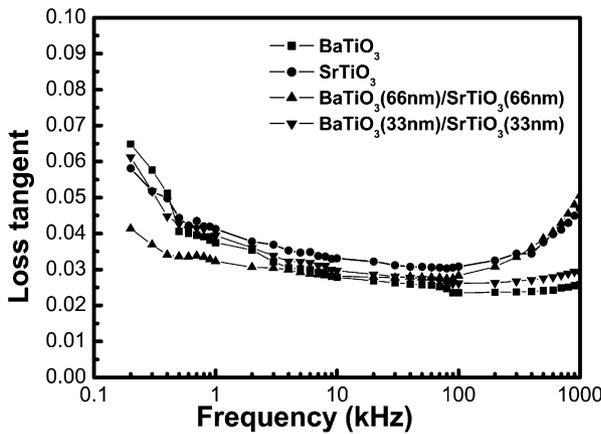


Fig. 5. The frequency dependence of the dielectric loss of all the films at room temperature.

the XRD patterns, which implies that the dielectric enhancement cannot be attributed to the changes in the film crystallinity and thickness. In this paper, each layer was crystallized at 750 °C for 8 min just after deposition, and then another layer was spin-coated onto the crystallized layer. Thus, the multilayered thin film can easily be formed by using this procedure, which can be seen from the XRD and AES results (shown in Figs. 1 and 2, respectively). As proposed by Catalan et al. [8], space

charges may be produced in the interface layer between BaTiO₃ and SrTiO₃, which will lead to the formation of the special layer of high conductivity, as compared with the bulk layer of BaTiO₃ or SrTiO₃ of low conductivity. The multilayered thin films consisting of two layers differing in electrical conductivity must give rise to the dielectric enhancement corresponding to the MW model [7,8]. Furthermore, the frequency dispersion of multilayered thin films may also be different from that of the uniform films due to the presence of the interface region.

The dielectric loss–frequency curve at room temperature of the thin film capacitors is shown in Fig. 5. At 10 kHz, the loss tangent of BaTiO₃, SrTiO₃, BaTiO₃ (33 nm)/SrTiO₃ (33 nm) and BaTiO₃ (66 nm)/SrTiO₃ (66 nm) were 0.0278, 0.0291, 0.0281 and 0.033, respectively. Dielectric loss increases slightly at the high and low frequency. The results above show that the loss tangent of multilayered thin films remained low compared with the uniform thin film, while dielectric constant was enhanced in the sol–gel derived BaTiO₃/SrTiO₃ multilayered thin films on Pt/Ti/SiO₂/Si substrate. This characteristic of multilayered thin films was different from that of epitaxial ferroelectric superlattices on oxide substrate. For epitaxial thin film, the dielectric enhancement is generally associated with high dielectric loss simultaneously and the stacking periodicity in which the dielectric enhancement can be observed

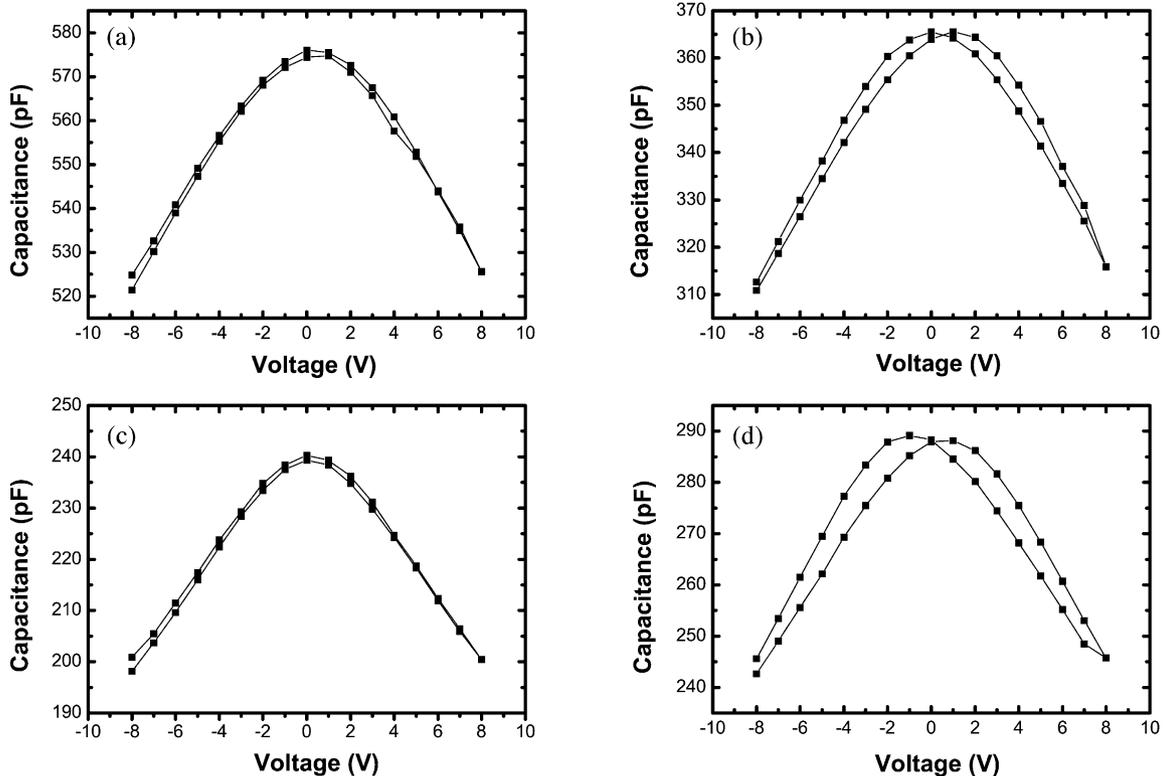


Fig. 6. The capacitance–voltage curves of (a) BaTiO₃ (33 nm)/SrTiO₃ (33 nm), (b) BaTiO₃ (66 nm)/SrTiO₃ (66 nm), (c) SrTiO₃ and (d) BaTiO₃ at 500 kHz.

is often small (< 10 nm). The difference of the interface of polycrystalline multilayered thin films and epitaxial ferroelectric superlattices may be attributed to the different phenomenon. The multilayered thin films reported in this paper were polycrystalline in nature. There were many grains and grain boundaries in the interface in each layer. Therefore, it is reasonable to assume that the thickness of the interface layer is larger than that in epitaxial dielectric superlattices, which may cause the larger stacking periodicity required for observing the dielectric enhancement. And the different nature of the interface layer may also cause the different characteristic of the dielectric loss.

Capacitance–voltage (C – V) curves of the films are shown in Fig. 6. This curve was measured at room temperature using a small AC signal of 10 mV at 500 kHz. The signal was applied across the sample, while the d.c. electric field was swept from positive to negative bias and back again. The C – V curves of BaTiO_3 and BaTiO_3 (66 nm)/ SrTiO_3 (66 nm) films had apparent hysteresis, while the C – V curves of SrTiO_3 and BaTiO_3 (33 nm)/ SrTiO_3 (33 nm) had no apparent hysteresis. The C – V curves of SrTiO_3 and BaTiO_3 indicate the deposited films were paraelectric and ferroelectric in nature, respectively. Due to the presence of the BaTiO_3 ferroelectric layer, the C – V curve of BaTiO_3 (66 nm)/ SrTiO_3 (66 nm) shows hysteresis. For BaTiO_3 (33 nm)/ SrTiO_3 (33 nm), the thickness of each BaTiO_3 layer was smaller than the critical size in which ferroelectricity can be exhibited, so no hysteresis can be observed.

4. Conclusions

Polycrystalline BaTiO_3 / SrTiO_3 multilayered thin films have been prepared on Pt/Ti/ SiO_2 /Si substrates by sol–gel processing, and compared with the uniform BaTiO_3 and SrTiO_3 films. The dielectric constant of the multilayered films was significantly enhanced and the dielectric loss was almost the same as that of the uniform thin films. At 1 kHz, the dielectric constants of BaTiO_3 , SrTiO_3 , BaTiO_3 (33 nm)/ SrTiO_3 (33 nm), and

BaTiO_3 (66 nm)/ SrTiO_3 (66 nm) is 348, 270, 422 and 660, and the loss tangents are all below 0.05. The frequency dispersion of the dielectric constant in the multilayered thin films is larger than that in the uniform films, and the capacitance–voltage relation of the multilayered thin films also show different characteristics with the uniform films. A mechanism of dielectric enhancement of the sol–gel derived multilayered thin films was suggested.

Acknowledgments

The authors wish to express their appreciation for the financial support from the Natural Science Foundation for youth of Jiangsu, China (grant no. BQ98037).

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