

Synthesis and Electrical Characterization of BaTiO₃ Thin Films on Si(100)

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ABSTRACT

BaTiO₃ thin film has been deposited on Si(100) substrate using sol-gel process and deposited by using spin – coating technique. The BaTiO₃/Si(100) structures were studied by structural and electrical characteristics. The X-ray diffraction of BaTiO₃/Si(100) shows that the diffraction peaks become increasing sharp with increasing calcination temperatures indicating the enhance crystallinity of the films. Scanning electron microscopy of BaTiO₃ thin films shows the crack free and uniform nature. The capacitance-voltage measurement of BaTiO₃ thin film deposited on Si(100) annealed at 600 °C shows large frequency dispersion in the accumulation region. The current-voltage measurement of BaTiO₃/Si shows the ideality factor was approaches to unity at 600 °C.

Keywords: Sol-Gel Technique, BaTiO₃ Thin Film, C-V, I-V

1. Introduction

Barium Titanate (BaTiO₃), a well-known dielectric material has been used as an insulating material to fabricate MIS structures. BaTiO₃ exhibits several advantages, properties such as high charge storage capacity, good insulating property, low leakage current density and high dielectric breakdown strength. It is also a potential material for active microwave tunable device because of its variable dielectric constant under external electric field. It has also been shown that BaTiO₃ works as an excellent buffer layer for YBa₂Cu₃O_{7- δ} high-T_c superconductor on various substrates, in particular Si and Al₂O₃ [1]. Recently, J. S. Lee *et al.* [2] fabricated n-MOSFET structures sequentially with the CMOS process and investigated the insulator characteristics, programming and resistance behaviour of BaTiO₃ films. BaTiO₃ are transparent in the visible and infrared [3] and possess strong electro-optic coefficients making them attractive for active and passive optical components.

BaTiO₃ thin film can be grown using pulsed laser deposition [4], chemical vapor deposition (CVD) [5], metal organic chemical vapour deposition [6-7], polymeric precursor method [8-11], sol-gel synthesis [12] and molecular beam epitaxy (MBE) [1,13]. MBE can be used to grow complex oxide thin film substrate with atomic layer accuracy [14]. High quality BaTiO₃ thin films are gener-

ally grown on lattice matched substrate such as MgO and SrTiO₃. Integration of BaTiO₃ thin film with silicon processing may enable the properties of ferroelectric to be utilized in combination with CMOS in multi material integration. Ion beam – assisted deposition of various template layers such as MgO and Ytria – stabilized zirconia has been used to develop thin film of super conducting YBa₂Cu₃O₇ as well as oriented layers of (Pb, Ba) TiO₃ [15,16].

In recent years, the sol-gel technique has gained interest in the area of processing of thin films because of the several advantages it offers, such as easier composition control, better homogeneity, low processing temperature and low equipment cost [17]. For the present investigations BaTiO₃ thin films have been deposited on Si(100) substrates using sol-gel technique through organic precursor route.

2. Experimental Details

(100) oriented Si wafers were well rinsed with warm acetone and methanol followed by etching in HNO₃/HF (1:1) for 1 minute. BaTiO₃ thin films were deposited on the polish side of the Si using sol-gel process.

Barium acetate (Sigma Aldrich, UK) and Titanium butoxide were used as a starting material. Barium acetate was dissolved in glacial acetate acid and reflux in a reflux condenser at a temperature of about 120°C for six

hours to obtain a clear solution, after obtaining a clear solution, Titanium butoxide was added in a proper mole ratio and the solution was stirred to get homogenous precursor. The viscosity of the solution was varied by the addition of 2-methoxy ethanol. The precursor solution was coated on Si(100) wafers by spin coating technique. The spin coating was done at the rate of 3000 rpm. The film was annealed at 300°C and 600°C for 30 minutes.

The focus of the present work is to study of BaTiO₃ thin films prepared by the sol gel technique and deposited by using spin – coating technique. The BaTiO₃/Si(100) structures were studied by structural and electrical characteristics. The crystalline nature and the phase formation of the deposited thin film were confirmed by power X-ray diffraction analysis using CuK_α radiation ($\alpha = 1.5418$ A.U.) surface morphology of the film were observed using scanning electron microscopy.

The C-V characteristics of the MIS diodes were measured at 1 MHz frequency at room temperature in the dark using a lock in amplifier (EG & G Model 5204). The ohmic contact was made on the back side of Si(100) by successive deposition of Au-Ge (2:1) alloy under a vacuum of 10⁻⁶ mbar and annealed at 400°C under argon atmosphere for 2 minutes.

3. Results and Discussion

The crystalline quality of BaTiO₃ precursor were prepared by sol-gel technique and deposited by using spin – coating technique. The **Figure 1** shows the XRD pattern of BaTiO₃ thin film on Si(100) substrate with different annealing temperatures. As deposited BaTiO₃ thin film and annealed at 300°C shows amorphous in nature. The crystalline behaviors of the deposited BaTiO₃ thin film annealed at 600°C shows sharp peaks indicating the enhance the crystallinity of the films. The structure of the BaTiO₃ thin film was found to be tetragonal.

Figure 2 show the FTIR spectra of BaTiO₃ thin films annealed at 600°C. The intense band at the edge of detection (260 cm⁻¹) is assigned to Ti-O mode in developed network [13]. The Figure shows that the broad and strong band observed at 450 cm⁻¹ characteristics of Ti-O bond.

Figure 3 (C1 & C2) shows the SEM micrograph of BaTiO₃ thin films annealed at 300°C and 600°C. The BaTiO₃ thin films deposited on Si(100) annealed at 300°C shows the agglomeration of the films shown in **Figure 3** (C1). The BaTiO₃ thin films deposited on Si(100) annealed at 600°C shows the films became crack free and uniform nature.

The electrical properties of BaTiO₃/Si(100) were studied by using 1 MHz capacitance-voltage characteristics. **Figures 4(a)** and **(b)** shows room temperature C-V characteristics for the sample annealed at 300°C and 600°C of BaTiO₃/Si(100). **Figure 4(a)** shows that the capacitance

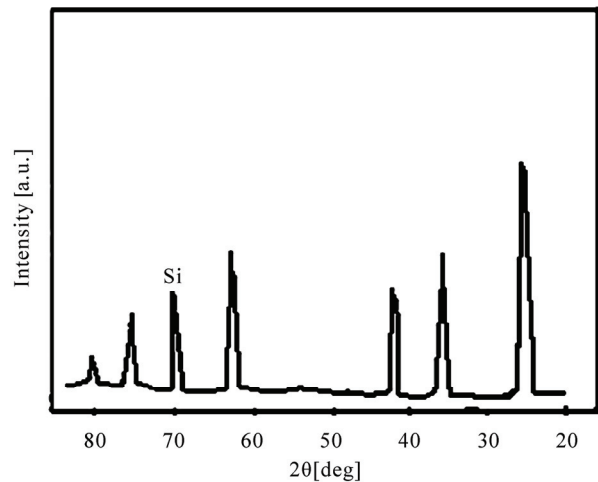


Figure 1. XRD pattern of BaTiO₃ thin film on Si(100) substrate annealed at 600°C.

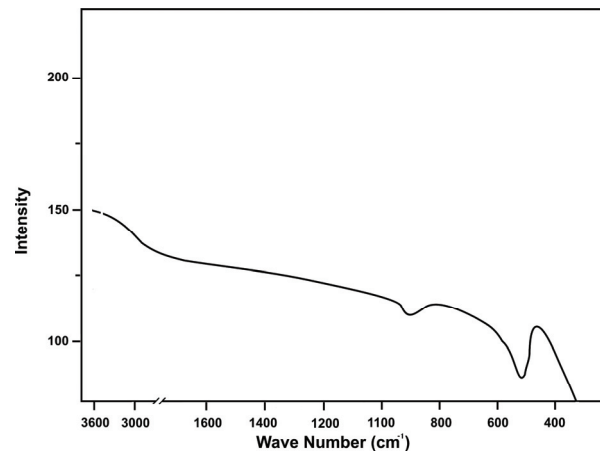


Figure 2. FTIR spectra of BaTiO₃ thin films annealed at 600°C.

remains unchanged with in that bias range. **Figure 4(b)** shows BaTiO₃ thin film deposited on Si(100) and annealed at 600°C showed large frequency dispersion in the accumulation region. The capacitance was changed from the inversion value to a value above flat band capacitance at 1 MHz. The electrical properties of BaTiO₃/Si(100) structure improved with annealing temp. at 600°C shown in **Figure 4(b)**. The result shows that the deposited BaTiO₃ insulator is good enough to use as gate insulator of MIS FET.

For 300°C annealed temperature, the C-V curve shows virtually flat which is an evidence of little modulation of the surface potential by the applied voltage, However when the film is subjected at 600°C annealing temperature the C-V plot shows a dramatic change in the 1 MHz freq. C-V behavior and considerable reduction in the frequency dispersion suggest a much closer approach to

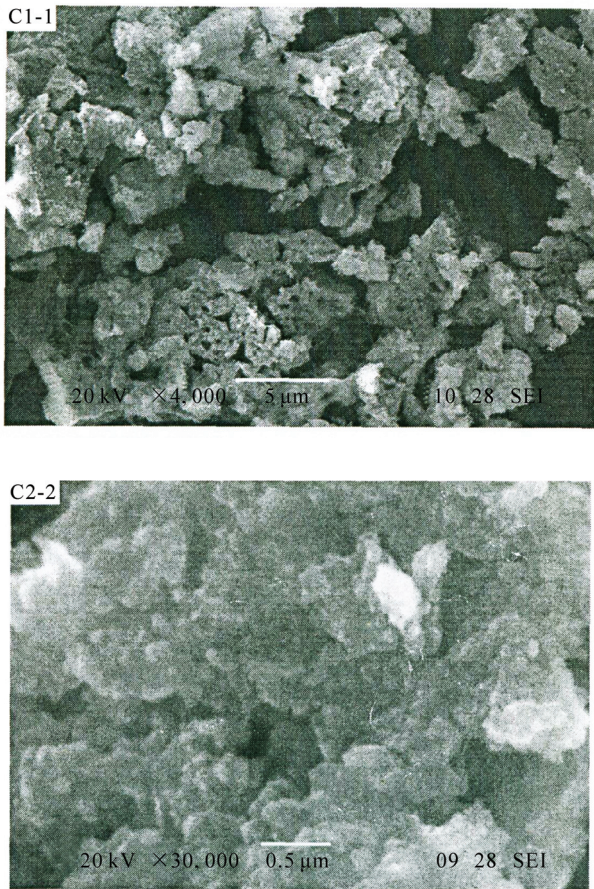


Figure 3. SEM of BaTiO₃ thin films annealed at (C1) 300°C and (C2) 600°C.

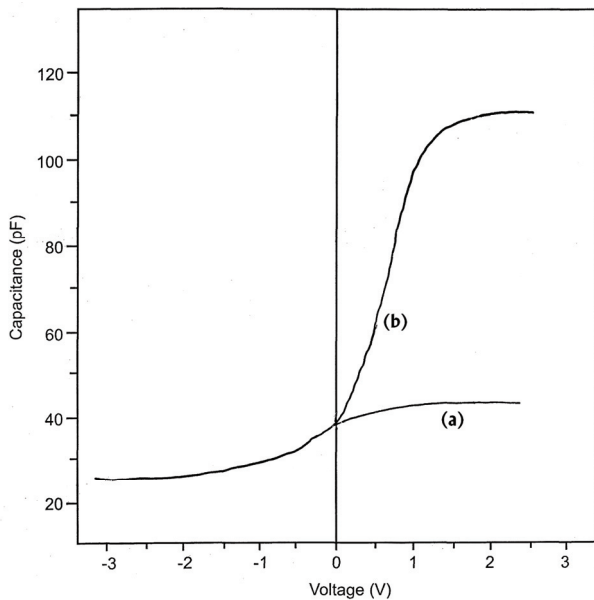


Figure 4. Capacitance-voltage characteristics of BaTiO₃/Si (100) annealed at (a) 300°C; (b) 600°C.

surface accumulation, *i.e.*, usually observed in the metal insulator semiconductor structure. Hence, the electrical properties of BaTiO₃/Si(100) MIS structure improved with annealing temperature at 600°C.

Figure 5 shows Current-Voltage (I-V) Characteristics of a typical diode with 90 Å thick BaTiO₃ film on Si (100). The room temp. Current-voltage characteristics were obtained to access the quality of deposited thin films. The forward bias current-voltage characteristics were measured and fitted to the equation

$$J = J_o \left(e^{qv/nKT} - 1 \right) \quad (1)$$

where J is the current density in amps/cm² and n is ideality factor of the diode. When n is close to unity, the results of thermionic emission theory are valid such that,

$$J_o = A^{**} T^2 \times e^{-\Phi/KT} \quad (2)$$

where A^{**} is the modified Richardson constant in amp/cm² and Φ – Barrier height.

The saturation current density J_s is given by

$$J_s = A^* T^2 \exp\left(-\frac{q\phi Bn}{kT}\right) \quad (4)$$

The parameter n is given by

$$n = \left[1 + \frac{\partial \Delta\phi}{\partial V} + \frac{kT}{q} \frac{\partial (\ln A^*)}{\partial V} \right]^{-1} \quad (5)$$

where ϕ is the height of Schottky barrier, $\Delta\phi$ is the Schottky barrier lowering and A^* is the effective Richardson constant.

For the annealing temperature at 300 and 600°C of BaTiO₃/Si shows the ideality factor was found to be varying

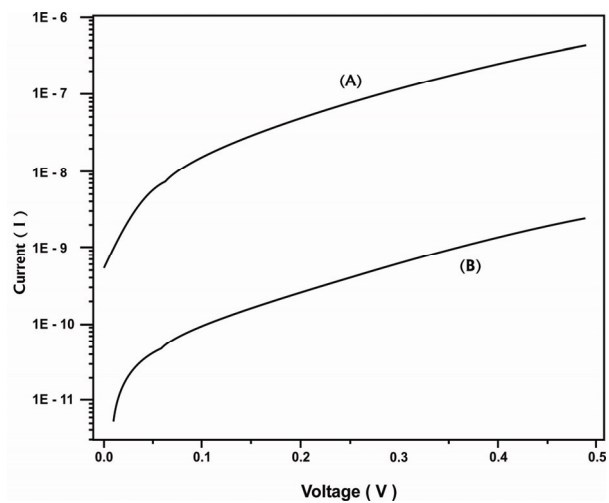


Figure 5. I – V Characteristics of a Typical diode with 90 Å thick BaTiO₃ film on Si (100) with annealed at (A) 300°C and (B) 600°C.

between 1.2 to 1.1. The value of $n = 1$ is consistent with current injection through a shottkey barrier, While large value indicates conduction by generation recombination. A Poor ideality factor can have variety of interpretation among them, the effect of Tunneling can be excluded because of low carrier density in substrates. The ideality factor decreases with increasing annealing temp. of BaTiO₃/Si as shown in **Figure 5**.

These results show that the electrical properties of BaTiO₃/Si, MIS structure improved at higher annealing temp.

4. Conclusions

BaTiO₃ thin film has been synthesized using sol-gel process and deposited on Si (100) by using spin – coating technique. The BaTiO₃/Si(100) structures were studied by structural and electrical characteristics. The XRD and SEM of BaTiO₃/Si(100) indicates the enhance crystallinity of the films with annealing temperature at 600°C. The C-V measurement of BaTiO₃ thin film deposited on Si(100) annealed at 600°C shows large frequency dispersion in the accumulation region. The current-voltage measurement of BaTiO₃/Si shows the ideality factor was approaches to unity at 600°C.

REFERENCES

- [1] S. Witanachi, S. Patel, D. T. Shaw and H. S. Kwok, "Effect of Buffer Layers on Low-Temperature Growth of Mirror-Like Superconducting Thin Films on Sapphire," *Applied Physics Letters*, Vol. 55, No. 3, 1989, pp. 295-297.
- [2] J. S. Lee, Y. H. Bae and Y. H. Lee, "A Novel BaTiO₃/SiO₂-Based Voltage-Programmable Link Applicable to On-Chip Programmable Devices," *Semiconductor Science and Technology*, Vol. 15, No. 3, 2000, pp. 267-269
- [3] A. Petraru, J. Schubert, M. Schmid and C. Buchal, "Ferroelectric BaTiO₃ Thin-Film Optical Waveguide Modulators," *Applied Physics Letters*, Vol. 81, No. 8, 2002, pp. 1375-1377.
- [4] T. Garcia, P. Bartolo-Pérez, E. de Posada, J. L. Peña and M. Villagrán-Muniz, "Studies of Pulsed Laser Deposition Processes of BaTiO₃ Thin Films," *Surface and Coatings Technology*, Vol. 201, No. 6, 2006, pp. 3621-3624.
- [5] T. T. W. Kim, Y. S. Yoon, S. S. Yom and C. O. Kim, "Ferroelectric BaTiO₃ Films with a High-Magnitude Dielectric Constant Grown on p-Si by Low-Pressure Metalorganic Chemical Vapor Deposition," *Applied Surface Science*, Vol. 90, No. 1, 1995, pp. 75-80.
- [6] X. D. Wu, A. Inam, M. S. Hegde, B. Wilkens, C. C. Chang, S. Miura, S. Matsubara, Y. Miyasaga and N. Shohata, "High Critical Currents in Epitaxial YBa₂Cu₃O_{7-x} Thin Films on Silicon with Buffer Layers," *Applied Physics Letters*, Vol. 54, No. 8, 1989, pp. 754-756.
- [7] D. K. Fork, F. A. Ponce, J. C. Tramontana and T. H. Geballe, "Epitaxial MgO on Si(001) for Y-Ba-Cu-O Thin-Film Growth by Pulsed Laser Deposition," *Applied Physics Letters*, Vol. 58, No. 20, 1991, pp. 2294-2296.
- [8] V. Agrawal and M. Liu, "Preparations of Barium Cerate-Based Thin Films Using a Modified Pechini Process," *Journal of Materials Science*, Vol. 32, No. 3, 1997, pp. 619-625
- [9] V. Bouquet, S. M. Zanetti, C. R. Foschini, E. R. Leite, E. Longo and J. A. Varela, In: N. P. Bansal, K. V. Logan and J. P. Singh, Eds., *Innovative Processing and Synthesis of Ceramic, Glasses, and Composites, Ceramic Transactions*, The American Ceramic Society Inc., Westerville, Vol. 85, 1998, p. 333.
- [10] S. M. Zanetti, E. R. Eite, E. Longo and J. A. Varela, "Preparation and Characterization of SrBi₂Nb₂O₉ Thin Films Made by Polymeric Precursors," *Journal of Materials Research*, Vol. 13, No. 10, 1998, pp. 2932-2935.
- [11] S. M. Zanetti, E. Longo, J. A. Varela and E. R. Leite, "Microstructure and Phase Evolution of SrTiO₃ Thin Films on Si Prepared by the Use of Polymeric Precursors," *Materials Letters*, Vol. 31, No. 3-6, 1997, pp. 173-178
- [12] L. Beckers, Y. Schubert, W. Zander, J. Ziesmann, A. Eckau, P. Leinenbach and C. Buchal, "Structural and Optical Characterization of Epitaxial Waveguiding BaTiO₃ Thin Films on MgO," *Journal of Applied Physics*, Vol. 83, No. 6, 1998, pp. 3305-3310.
- [13] S. Kwak, K. Zhang, E. P. Boyd, A. Erbin, B. J. Wilkens, "Metalorganic Chemical Vapor Deposition of BaTiO₃ Thin Films," *Journal of Applied Physics*, Vol. 69, No. 2, 1991, pp. 767-772.
- [14] M. E. Naggar, D. A. Boyd and D. G. Goodwin, "Characterization of Highly-Oriented Ferroelectric PbxBa_{1-x}TiO₃," *Journal of Material Research*, Vol. 20, No. 11, 2005, pp. 2969-2976.
- [15] L. A. Wills, B. W. Wessels, D. S. Richeson and T. J. Marks, "Epitaxial Growth of BaTiO₃ Thin Films by Organometallic Chemical Vapor Deposition," *Applied Physics Letters*, Vol. 60, No. 1, 1992, pp. 41-43.
- [16] Lemoine, B. Gilbert, B. Michanx, J. P. Pirad and A. J. Leclux, "Synthesis of Barium Titanate by the Sol-Gel Process," *Journal of Non-Crystalline Solids*, Vol. 175, No. 1, 1994, pp. 1-13.
- [17] M. Burgos and M. Langlet, "The Sol-Gel Transformation of TIPT Coatings: A FTIR Study," *Thin Solid Films*, Vol. 349, No. 1-2, 1999, pp. 19-23.