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Properties of $BaBi_2Ta_2O_9$ thin films prepared by chemical solution deposition technique for dynamic random-access memory applications

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We report on the properties of $BaBi_2Ta_2O_9$ (BBT) thin films for dynamic random-access memory (DRAM) and integrated capacitor applications. Crystalline BBT thin films were successfully fabricated by the chemical solution deposition technique on Pt-coated Si substrates at a low annealing temperature of 650 °C. The films were characterized in terms of structural, dielectric, and insulating properties. The electrical measurements were conducted on Pt/BBT/Pt capacitors. The typical measured small signal dielectric constant and dissipation factor, at 100 kHz, were 282 and 0.023, respectively, for films annealed at 700 °C for 60 min. The leakage current density of the films was lower than 10^{-9} A/cm^2 at an applied electric field of 300 kV/cm. A large storage density of 38.4 fC/μm^2 was obtained at an applied electric field of 200 kV/cm. The high dielectric constant, low dielectric loss and low leakage current density suggest the suitability of BBT thin films as dielectric layer for DRAM and integrated capacitor applications.

I. INTRODUCTION

High dielectric constant materials are being explored for the next generation of high-density dynamic random-access memory (DRAM) applications because of the physical thickness limit of oxide/nitride based capacitance materials currently being used. The parameters of importance for DRAM applications are dielectric constant and leakage current characteristics. The high dielectric constant materials are desirable, as they will lead to simple capacitor design and charge storage density comparable to conventional dielectrics even at much larger thickness. A low leakage current density is necessary to reduce the refreshing time. Dielectric materials such as Ta_2O_5 and $Ba_xSr_{1-x}TiO_3$ (BST) have been widely investigated for DRAM applications. Ta_2O_5 is the most suitable material from a fabrication compatibility point of view; however, it has been unable to match the leakage current characteristics of conventional dielectrics. BST offers the advantage of very high dielectric constant; however, it has to overcome the problems of high leakage current in addition to processing and integration issues.

In the present research, we have investigated the properties of $BaBi_2Ta_2O_9$ (BBT) thin films as an alternative dielectric material for DRAM applications. BBT material belongs to the layered-perovskite family and crystallizes in the orthorhombic phase. A high dielectric constant of 400 has been reported for bulk-BBT material.[1] The high dielectric constant of BBT makes it attractive for DRAM and integrated capacitor application. It shows a diffused phase transition and has a Curie temperature of about 110 °C. BBT is expected to show more stable dielectric characteristics in the temperature range 25–100 °C compared to BST because of higher Curie temperature and diffused phase transition. A limiting factor for any DRAM capacitor is leakage current. In a 1T-1C DRAM cell, the stored charge on the storage capacitor leaks off with time through various leakage mechanisms. This means that the DRAM cell must periodically be taken out of operation so that the stored charge can be refreshed.[2] Thus, the leakage current characteristics of the storage capacitor dielectric are very important in a 1T-1C cell. Paz de Araujo *et al.*[3] reported the importance of Bi-layered-perovskite compounds mainly as low leakage current materials. Additionally, Bi-layered-perovskite compounds are attractive for direct integration on silicon substrates for high-density electronic applications, because of the possibility of the formation of conducting Bi/Si interfacial layer. Here we report on the structural, dielectric, and leakage current characteristics of BBT thin films fabricated by chemical solution deposition technique (CSD).

II. EXPERIMENTAL

Thin films of $BaBi_2Ta_2O_9$ were prepared by CSD using room temperature processed alkoxide-carboxylate

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precursor solution. CSD processing has been extensively used in thin film technology because of easier composition control, good homogeneity, and uniform deposition over a large substrate surface area.[4] For the preparation of $BaBi_2Ta_2O_9$ thin films, barium acetate $(BaOOCCH_3)_2$ (Alfa), bismuth 2-ethylhexanoate $[Bi(C_7H_{15}COO)_3]$ (Alfa), and tantalum ethoxide $[Ta(OC_2H_5)_5]$ (Inorgtech) were chosen as precursors, and acetic acid, 2-ethylhexanoic acid, and 2-methoxyethanol were selected as solvents. Bismuth 2-ethylhexaonate and barium acetate precursors were dissolved in 2-ethylhexanoic acid and acetic acid, respectively, under room temperature conditions. These solutions were then added to the solution of tantalum ethoxide in 2-methoxyethanol. The final solution was stirred for about 2 h before coating. The precursor solution was filtered through 0.2 μm syringe filters and then spin-deposited onto Pt-coated Si substrates at 6000 rpm for 40 s. After deposition, films were kept on a hot plate (at ~350 °C) in air for 10 min to remove the solvents and other organics, and this step was repeated after each layer of coating to ensure complete removal of volatile matter. The post-deposition annealing of the films was carried out in a furnace at different temperatures for one hour under oxygen environment.

The thickness of the films was measured by variable angle spectroscopy ellipsometry (VASE). The structure of thin films was analyzed by x-ray diffraction (XRD). The diffraction patterns were recorded on a Scintag XDS 2000 diffractometer at a scanning speed of 2° 2θ/min using Cu K_α radiation at 40 kV. The surface morphology of the films was analyzed by Digital Instrument's Dimension 3000 atomic force microscope (AFM) using tapping mode with amplitude modulation. The electrical measurements were conducted on films in a metal-insulator-metal (MIM) configuration using Pt as the top and bottom electrodes. The top electrodes, area $= 3.1 \times 10^{-4}$ cm^2, were deposited on the top surface of films by sputtering through a shadow mask. The films were annealed at 650 °C for 20 min after top electrode deposition to ensure good electrical contact. The dielectric properties were measured with HP 4192A impedance analyzer at room temperature, and the leakage current versus voltage characteristics were measured by means of a Keithley 617 electrometer/source. The film properties were found to be strongly dependent on the excess Bi content and the best results were obtained for films with 10% excess Bi content. So this paper focuses on the properties of BBT thin films with 10% excess Bi content.

III. RESULTS AND DISCUSSION

The pyrolyzed films at 350 °C were found to be amorphous, and post-deposition annealing was required to develop crystallinity. Figure 1 shows the XRD patterns of BBT thin films as a function of annealing temperature. The films annealed up to 600 °C were found to be amorphous. As the annealing temperature was increased to 650 °C, a crystalline phase was obtained with peaks attributable to orthorhombic phase. The crystallization of the BBT phase was analyzed based on $BaBi_2Nb_2O_9$ (Powder Diffraction File Card No. JCPDS #12-0403), which also belongs to the layered-perovskite family, and crystallizes in the orthorhombic phase.[5] As the annealing temperature was increased, the peak intensity and sharpness were found to increase, indicating better crystallinity and an increase in grain size with temperature. The microstructure of BBT thin films was analyzed by atomic force microscope (AFM), and Fig. 2 shows the microstructure of the films annealed at 650 and 700 °C. The film annealed at 650 °C showed a smooth surface with very small crystallites while a well-defined grain structure was obtained at an annealing temperature of 700 °C.

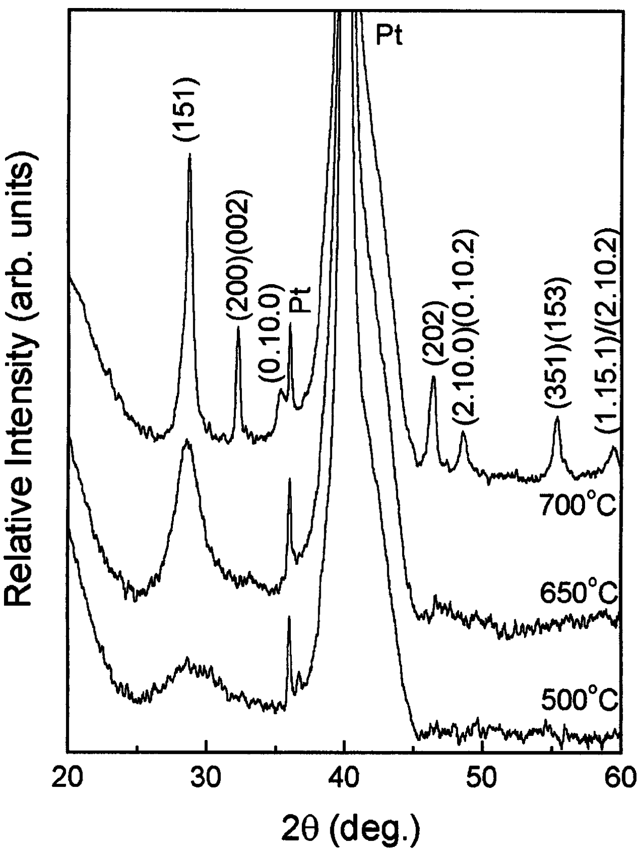

FIG. 1. X-ray diffraction patterns of $BaBi_2Ta_2O_9$ thin films annealed at different temperatures for 60 min.

The dielectric measurements were conducted on Pt/BBT/Pt capacitors by applying a small ac signal of 10 mV amplitude across the samples. The dielectric properties were found to be strongly dependent on the excess Bi content and the post-deposition annealing temperature. Table I summarizes the effect of excess

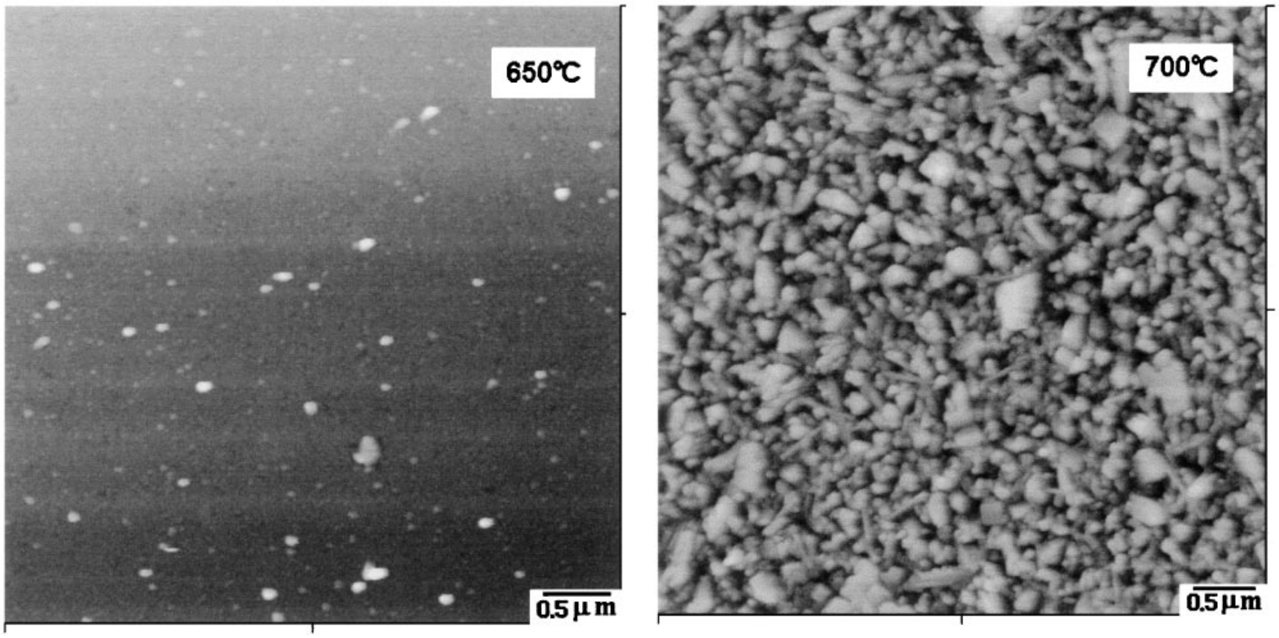

FIG. 2. AFM micrograph of $BaBi_2Ta_2O_9$ thin films annealed at 650 and 700 °C for 60 min (5 × 5 μm).

bismuth on the dielectric properties of BBT thin films annealed at 650 and 700 °C. The dielectric constant was found to increase with an increase in Bi content, and a maximum was obtained for samples with 10% excess Bi content. The measured small ac signal dielectric constant and dissipation factor, for films with 10% excess bismuth content and annealed at 700 °C for 60 min, were 282 and 0.023, respectively. The dissipation factor did not show any appreciable dependence on excess Bi content and was in the range 0.009–0.025 for films annealed at 700 °C for 60 min. The dielectric constant was found to decrease with further increase in Bi content beyond 10%, which may possibly be due to formation of a low dielectric constant bismuth oxide phase, even though no secondary phase was observed in XRD patterns for films with up to 20% excess Bi content. The dielectric constant was found to increase with increase in annealing temperature, which was predominantly due to improvement in crystallinity and grain size of the films. Figure 3 shows the behavior of dielectric constant and dissipation factor as a function of frequency. The permittivity showed no appreciable dispersion with frequency up to about 1 MHz, indicating that the values were not masked by any surface layer effects or electrode barrier effects. As the frequency was increased above 1 MHz, the dielectric constant was found to decrease and the loss factor was found to increase with frequency. This behavior was

TABLE I. Dielectric constant and dissipation factor (tan δ) as a function of annealing temperature and excess bismuth content.

	T = 650 °C		T = 700 °C	
Excess Bi (%)	ϵ_r	tan δ	ϵ_r	tan δ
0	46.5	0.001	62.7	0.009
5	54.3	0.002	94.9	0.020
10	57.8	0.003	282.6	0.023
15	56.2	0.002	211.2	0.021
20	67.8	0.003	189.6	0.022

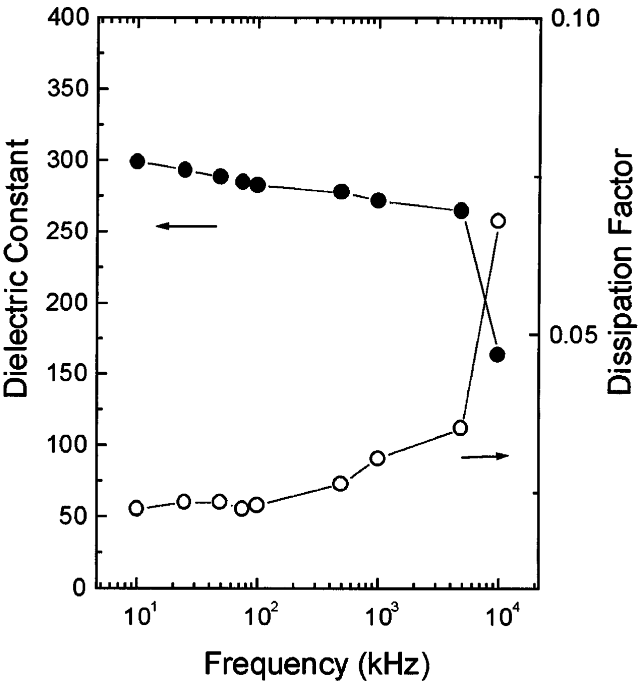

FIG. 3. Dielectric constant and dissipation factor as a function of frequency for a 0.2 μm-thick $BaBi_2Ta_2O_9$ film annealed at 700 °C for 60 min.

found to be extrinsic in nature as similar behavior was observed at around the same frequency for thin films of other dielectric materials. At frequencies of the order of a few MHz, the stray inductance L of the contacts and wires and/or the presence of a finite resistance in series with the films, which may arise due to intrinsic or extrinsic sources, may cause such behavior.[6] The high dielectric constant and low dielectric loss characteristics show the suitability of $BaBi_2Ta_2O_9$ thin films as the insulating dielectric layer for large value capacitors for various electronic devices.

For DRAM applications, a material with high dielectric constant and good insulating characteristics is required. A limiting factor for any DRAM capacitor is leakage current. In a DRAM cell, the stored charge capacitor leaks off with time through various leakage mechanisms which requires periodic refreshing of the stored charge. So the leakage current characteristics of the storage capacitor dielectric are very important for DRAM applications. The leakage current characteristics were measured using a Keithley 617 test system by applying dc voltages on Pt/BBT/Pt capacitors with a step height of 0.5 V and a delay time of 30 s. The results are shown in Fig. 4, in terms of leakage current density versus electric field characteristics of a 0.2 μm thick film with 10% excess bismuth content and annealed at 700 °C for 60 min. The leakage current densities of the films were lower than 10^{-9} A/cm^2 up to an applied electric field of 300 kV/cm, indicating good insulating characteristics. Another parameter of importance for DRAM applications is charge storage density. $BaBi_2Ta_2O_9$ can offer an order of magnitude higher charge storage density, at relatively larger thicknesses, in a DRAM cell capacitor compared to other gate dielectric materials such as SiO_2 ($\epsilon_r = 3.9$) and Ta_2O_5 ($\epsilon_r = 22$).[7] For DRAM techniques, the attempt is to retain high charge storage density by optimizing the capacitor parameters such as thickness and electrode area. For BBT thin films annealed at 700 °C, the charge storage density, defined by $Q_c = \epsilon_0 \epsilon_r E$, was calculated from C-V measurements on MIM capacitors. Here, E is the applied electric field. The C-V plots were obtained by applying a small ac signal of 10 mV amplitude and 100 kHz frequency across the sample while the dc electric field was swept from a positive bias to a negative bias and back again. Figure 5 shows the relation between the charge storage density and the applied electric field for a 0.2 μm thick film. The charge storage density was 38.4 fC/μm^2 at an applied electric field of 200 kV/cm. At this bias the leakage current density was of the order 10^{-10} A/cm^2. These values appear to be consistent with

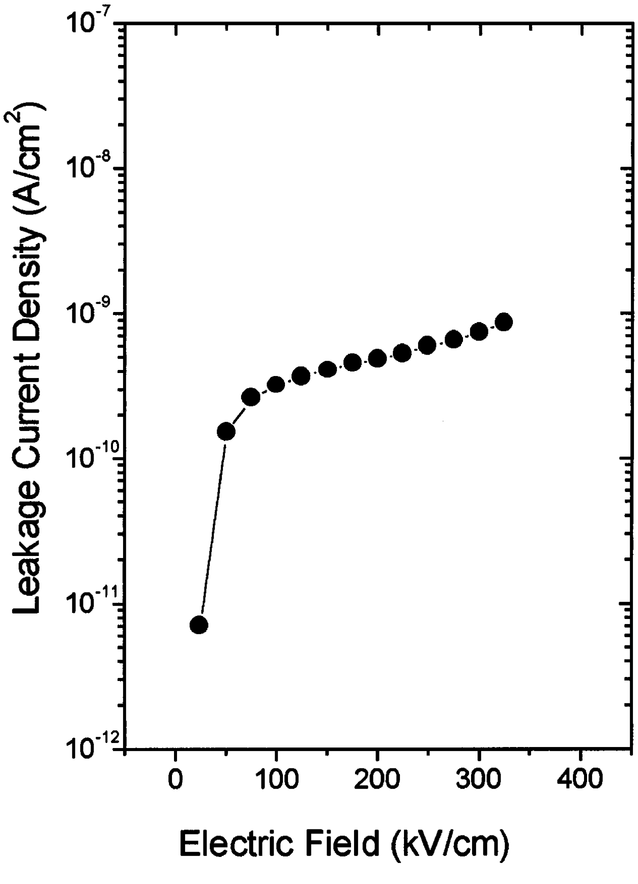

FIG. 4. Leakage current density versus applied electric field characteristics for a 0.2 μm-thick $BaBi_2Ta_2O_9$ film annealed at 700 °C for 60 min.

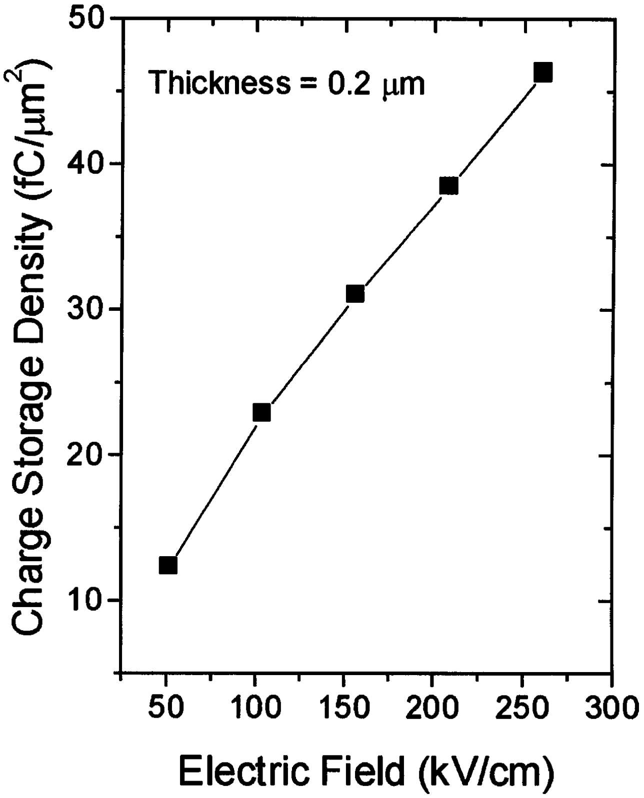

FIG. 5. Charge storage density as a function of applied electric field.

the projected requirements for a DRAM cell capacitor with density beyond 64 Mbit.

IV. CONCLUSION

In conclusion, thin films of $BaBi_2Ta_2O_9$ with crystalline structure were successfully prepared by chemical solution deposition technique on Pt-coated Si substrates at an annealing temperature of 650 °C. The BBT thin films were characterized for electrical properties in terms of dielectric and leakage current characteristics. The film properties were found to be strongly dependent on the excess Bi content and annealing temperature. The best results were obtained for films with 10% excess Bi content. Typical measured small signal dielectric constant and dissipation factor at 100 kHz were 282 and 0.023, respectively, for films annealed at 700 °C for 60 min. The leakage current density was lower than 10^{-9} A/cm^2 up to an applied field of 300 kV/cm. A charge storage density of 38.4 fC/μm^2 was obtained at an applied field of 200 kV/cm. The high dielectric constant, low dielectric loss, low leakage current density, and high charge storage density suggest the suitability of $BaBi_2Ta_2O_9$ thin films as capacitor dielectric layer for microelectronic applications.

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