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Ferroelectric Strontium Bismuth Tantalate Thin Films Deposited by Metalorganic Chemical Vapour Deposition (MOCVD)

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Abstract

Thin films of $Sr_{1-x}Bi_{2+x}Ta_2O_9$ (SBT) have been deposited by metalorganic chemical vapor deposition (MOCVD) on 150 mm Si wafers with Pt/Ti electrodes. The choice of Bi precursor significantly affects the process; film homogeneity is significantly improved when using a β*-diketonate Bi precursor in combination with compatible Sr and Ta precursors. A highly repeatable process has been developed, with good run-to-run composition and thickness control. Effects of Bi volatility have been investigated in annealing experiments that show the onset of Bi loss at ~570°C at reduced pressure (1–10 Torr). Film properties relevant to integrated ferroelectric random access* (Fe RAMS) *memories have also been characterized. Remenant polarizations ($2P_r$) up to 24* μ*C cm^{-2} have been obtained at 5 V, with 90% saturation of $2P_r$ at 1·5 V and a coercive voltage of 0·52 V for a 140 mn film. Electrical leakage current density values were $< 2\times10^{-8}$ A cm^{-2} at 1·5 V. Fatigue endurance has been measured to 10^{11} cycles with < 10% degradation in switched charge.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, ferroelectric properties, perovskites, tantalates, FeRAM.

1 Introduction

The development of ferroelectric films for memory applications continues at a rapid pace. Among many current issues, a stable process module to produce high quality, thin ferroelectric films for high density memories is needed. A number of ferroelectric materials are under consideration for FeRAMs, including Pb(Zr,Ti)O_3 (PZT) and $SrBi_2Ta_2O_9$ (SBT).[1,2] SBT has several potential advantages, including low switching field (which is independent of film thickness), high fatigue endurance with Pt electrodes, and rapid saturation of switched charge with applied field. Control of composition of the ferroelectric film is critical towards achieving optimal properties. Further, high density memory devices will require processes scalable to 200–300 mm wafer sizes and the capability to produce highly conformal ferroelectric thin films to evenly cover electrodes with aspect ratios >1. Metalorganic chemical vapor deposition (MOCVD) offers the ability to deposit high quality films, is scalable to large areas, and has a high level of conformality. MOCVD has been investigated by several groups for SBT[3–5] using aryl compounds for Bi. We have developed an MOCVD process[6,7] with a unique set of precursors that allows a high degree compositional control combined with low temperature processing (where conformality is generally highest). At the same time, good deposition rates have been preserved (which often decrease when kinetics are controlled by surface reactions). This paper contrasts the behavior of MOCVD processes based on conventional Bi precursors from the aryl family with that using a β-diketonate Bi source.

2 Experimental

SBT films were deposited at reduced pressure using two different sets of metalorganic precursors in solution. Deposition conditions and precursors are listed in Table 1. The films were deposited in a

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Varian High K CVD reactor using an ATMI LDS-300B liquid delivery system. Substrate temperature was calibrated using a platinum coated Si wafer instrumented with type R thermocouples. Composition and thickness were measured with a Rigaku 3613 wavelength dispersive X-ray fluorescence (WD-XRF) system. X-ray diffraction (XRD) was performed in the Bragg-Brentano ($\theta-2\theta$) geometry with a Rigaku Dmax diffractometer using CuK_α radiation and a graphite crystal monochrometer. Fourier transform infrared (FTIR) spectroscopy was performed in a grazing incidence reflection configuration to check for the presence of metal carbonates in films deposited at low temperature by infrared absorptance using a Perkin–Elmer 1600 FTIR spectrometer. For electrical characterization, Pt top electrodes were deposited through a shadow mask by electron-beam evaporation. Polarization was characterized with a Radiant Technologies RT6000 using virtual ground mode. Fatigue was measured with the same system using a square wave at 1 MHz. Electrical leakage was characterized using a stepped I–V technique in 0.5 V increments with 5 s hold time/voltage step and measuring average current for the last 1 s of each step.

3 Results and Discussion

A series of deposition experiments were performed with each precursor set scanning deposition temperature at 1 Torr total pressure. For precursor set 1, Sr and Ta incorporation efficiency (defined as the amount of a particular metal specie incorporated into a film divided by the amount of that specie delivered into the vaporizer) was relatively independent of temperature between 500 and 600 °C (Fig. 1). Bi showed a marked decrease in incorporation efficiency with temperature, dropping to nearly zero around 500°C. This range could be extended to slightly lower temperature with increased pressure. However, control of composition throughout the entire temperature range was very difficult. There are two factors that contribute to this. First, Bi becomes volatile at temperatures above 550 °C at reduced pressures. This is shown in Fig. 2, where the Bi content of an SBT film, determined by WD-XRF, is shown after several sequential annealing treatments in flowing Ar. (The experiment was conducted in a stepwise manner, annealing at the lowest temperature and highest pressure first, followed by lower pressure at the same temperature before raising the annealing temperature.) The second factor that caused difficulties in composition control was a tendency toward segregation in the SBT films using precursor set 1 (Fig. 3). At high substrate temperature, significant Bi is incorporated, but the composition of the film is far from stoichiometry. As substrate temperature drops, Bi content also decreases, but Bi-rich regions formed which were separated by areas of film containing only Sr and Ta oxide. Adjusting pressure and precursor ratios allowed deposition of films that were stoichiometric on the scale of XRF measurement (32 mm), but still also strongly segregated. Furthermore, the process was

Table 1. Deposition parameters and metalorganic precursors

Deposition system parameters	
Deposition temperature	330–600 °C
Total pressure	1–10 Torr
Oxygen content	0–80%
Substrate	Pt(100 nm)/Ti(10 nm)/Si
Metalorganic precursors	
Set 1	Triphenyl Bi [$Bi(Ph)_3$]
	Bis-tetramethylheptanedionato, Sr-tetraglyme adduct ($Sr(thd)_2$-tetraglyme)
	Tetrakis-isopropoxy tetramethylheptanedionato Ta [$Ta(OiPr)_4(thd)$]
Set 2	Tris-tetramethylheptanedionato Bi [$Bi(thd)_3$]
	Bis-tetramethylheptanedionato Sr-pentamethyldiethylenetriamine adduct [$Sr(thd)_2$-pmdeta]
	Tetrakis-isopropoxy tetramethylheptanedionato Ta [$Ta(OiPr)_4(thd)$]

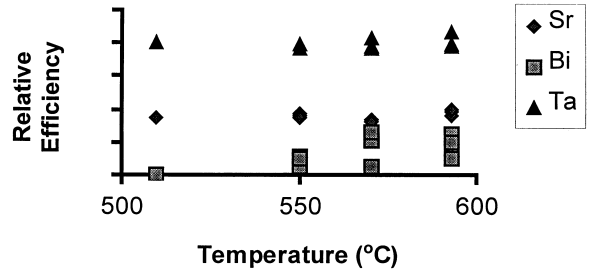

Fig. 1. Variation of incorporation efficiency versus temperature for precursor set 1 [$Bi(Ph)_3$].

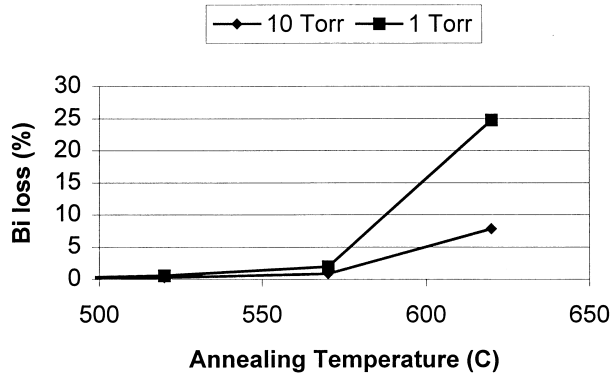

Fig. 2. Bi loss from a Bi-rich SBT annealed sequentially at reduced pressure in flowing Ar. Measurement precision by WD-XRF was $\sim 0{\cdot}5\%$.

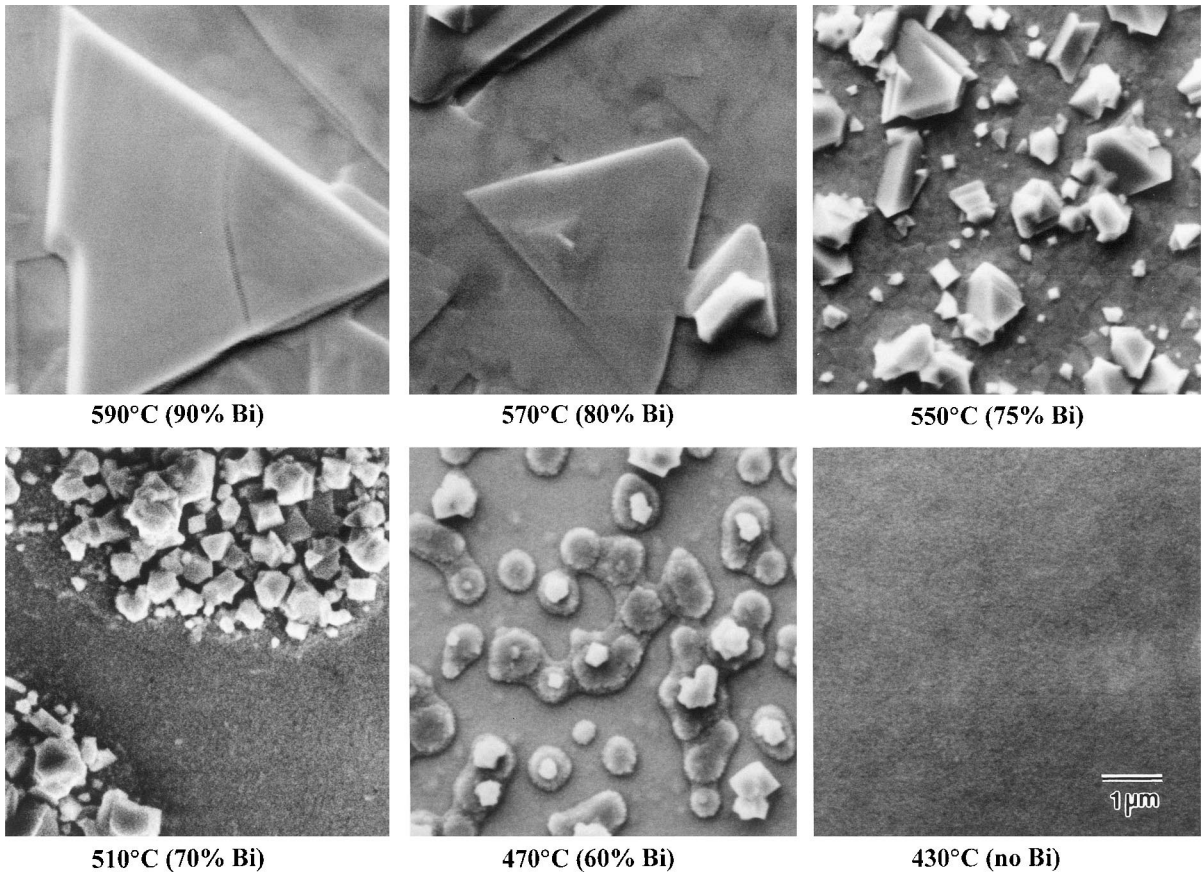

Fig. 3. Film morphology as a function of deposition temperature using precursor set 1[$Bi(Ph)_3$]. Average Bi content as measured by WD-XRF is indicated. Crystalline features are Bi-rich.

extremely difficult to repeat, with wide variations in stoichiometry for conditions that yielded films with reasonable compositions.[6,7]

Changing the Bi source to $Bi(thd)_3$ (precursor set 2) allowed the process to be carried out at temperatures below 430°C with significantly improved process repeatability and conformality of approximately 90% on 1:1 aspect ratio features of 0·5 μm size.[6,7] Film morphology also improved markedly, with a smoothness similar to the low temperature film, in Fig. 3. The difference in the two processes is attributed to the fact that $Bi(Ph)_3$ is relatively thermally stable and does not decompose at low temperature. In contrast, $Bi(thd)_3$ behaves much more like the Sr and Ta β-diketonate and mixed alkoxide-β-diketonate precursors, respectively.

Carbon incorporation is often a concern for films produced from metalorganic precursors. This issue is generally much diminished for oxide films because of the use of oxygen as a co-reactant. IR absorptance of several films, shown in (Fig. 4), revealed no evidence for metal carbonate[8,9] formation. In the absence of added oxygen during the deposition process, it was found that the film displayed a darkened appearance, which is evident in the FTIR spectrum as broadband absorption above 800 cm^{-1}. This suggests some carbon incorporation in the absence of oxygen as a co-reactant. Adding

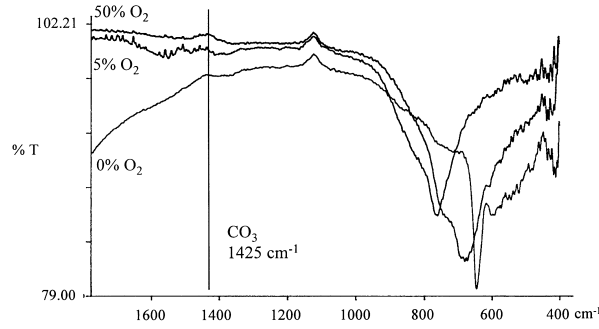

Fig. 4. Grazing angle incidence FTIR spectra from SBT films deposited at 385°C with varying amounts of O_2 as a co-reactant using precursor set 2 [$Bi(thd)_3$]. No $SrCO_3$ was observed in the films.

even a small amount of oxygen (5%), eliminated this absorptance. We note that the location and sharpness of the M–O modes changed among the different films. We attribute this to shifts in composition of the metal cations with different proportions of O_2 co-reactant and the formation of more discrete M–O species.

Further evidence for purity of the thin films deposited from precursor set 2 was found in other physical and electrical properties. After annealing at 750–800 °C for 1 h, the films had the desired Aurivillius crystal structure, which was confirmed by XRD (Fig. 5). High resolution TEM showed the films had well developed layered pseudo-perovskite

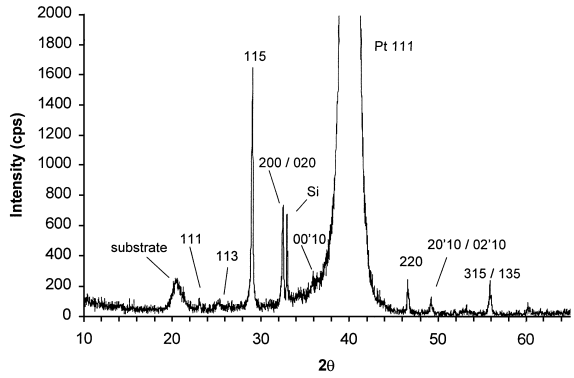

Fig. 5. XRD pattern from SBT deposited using precursor set 2 after 750°C post anneal for 1h.

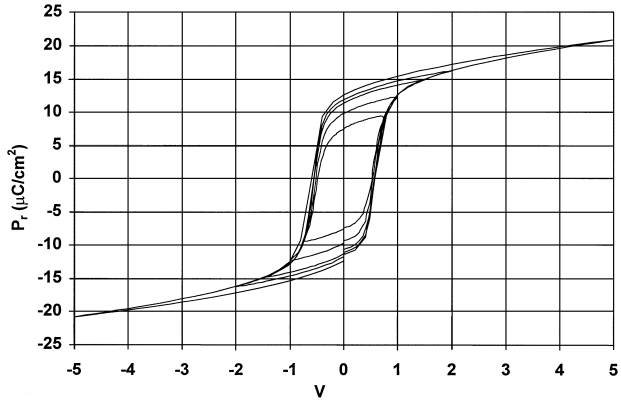

Fig. 6. Ferrroelectric hysteresis from an SBT film deposited below 430°C using precursor set 2 and post annealed in flowing O_2 at 800°c for 1h.

structure. Ferroelectric properties for thin films (140 nm) were very good (Fig. 6) with remenant polarization ($2P_r \sim 24\,\mu C\,cm^{-2}$). The films had low coercive voltage (0·52 V) which corresponds to a low coercive field ($38\,kV\,cm^{-1}$) and well saturated polarization by 1·5 V. Electrical fatigue endurance was also quite good, showing less than 10% decrease in switched polarization at 10^{11} cycles. Current–voltage (I–V) characteristics showed electrical leakage $< 2\times10^{-8}\,A\,cm^{-2}$ for applied voltage ≤ 2 V ($\sim 4\,V_c$). These results demonstrate that these films are suitable for low voltage operation (1·5 V) in ferroelectric memories.

4 Conclusions

Process effects were examined for two sets of metalorganic precursors for the MOCVD of SBT thin films. A process based on triphenyl Bi [$Bi(Ph)_3$] was difficult to control due to Bi segregation and required high temperatures ($T \geq 470$°C) for sufficient Bi incorporation. A process using $Bi(thd)_3$ permitted deposition at lower temperatures with significantly improved morphology and no measurable carbon content by FTIR when O_2 was used as a co-reactant. Films produced with this process had high values of remenant polarization ($2P_r \sim 24\,\mu C\,cm^{-2}$) and good fatigue endurance ($P_{SW} > 90\%$ of the initial value at 10^{11} cycles).

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