Laser Annealing of Ferroelectric $SrBi_2Ta_2O_9$, $Pb(Zr_XTi_{1-X})O_3$ and $CeMnO_3$ Thin Films

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ABSTRACT

Excimer laser annealing studies were conducted of $SrBi_2Ta_2O_9$, $Pb(Zr_xTi_{1-x})O_3$ and $CeMnO_3$ thin films. The main incentive was to develop a low temperature process for $SrBi_2Ta_2O_9$ thin films, which typically require a 750 C anneal to crystallize and achieve optimum ferroelectric properties. The results show that room temperature laser annealing can crystallize $SrBi_2Ta_2O_9$, with a strong (200) preferred orientation. The $Pb(Zr_xTi_{1-x})O_3$ and $CeMnO_3$ thin films investigated in this study were crystalline as deposited. Laser annealing of the $Pb(Zr_xTi_{1-x})O_3$ and $CeMnO_3$ films did not result in a significant increase in crystallinity, as evidenced by the intensities of the x-ray diffraction peaks. Electrical characterization of laser annealed $SrBi_2Ta_2O_9$ thin films showed good dielectric properties and the onset of ferroelectric behavior. Low temperature laser annealing is shown to be a viable approach to enable integration of ferroelectric $SrBi_2Ta_2O_9$ films with silicon based micro-electronics, for ferroelectric memory applications.

INTRODUCTION

Ferroelectric random access memory (FeRAM) devices offer the potential for high-speed and low-voltage operation, as compared to traditional non-volatile memory devices, such as flash memory and EEPROM [1]. FeRAM technology is currently being developed for both stand alone memory products and embedded memory for logic devices [2]. $SrBi_2Ta_2O_9$ (SBT) and $Pb(Zr_xTi_{1-x})O_3$ (PZT) are presently the leading contenders for the ferroelectric material in FeRAM applications [3]. Cerium manganese oxide (CMO) is a promising new ferroelectric material, which is presently being investigated. Of these materials, PZT is the most well established technology. SBT offers the potential for lower voltage operation and better fatigue performance than PZT [4]. However, SBT films require a post deposition anneal of 700 C to 800 C in an oxidizing environment, in order to achieve optimum ferroelectric properties [5]. This high temperature anneal step is incompatible with present silicon CMOS fabrication.

In this work, we investigated the use of excimer laser annealing, to selectively heat and crystallize ferroelectric oxide thin films on silicon substrates. We focused our investigation on SBT, since there is an immediate need for low temperature processing of SBT for FeRAM applications. For PZT, It is well established that thin films can be prepared with suitable ferroelectric properties at temperatures below 550 C [5]. Crystalline CMO thin films have also been prepared at Structured Materials Industries, at temperatures compatible with silicon processing. Excimer laser annealing of PZT and CMO thin films is being investigated in this work to see if further improvements in crystallinity or ferroelectric properties can be achieved.

Thin films of ferroelectric materials such as SBT, PZT and CMO can be prepared by a variety of deposition techniques, including sputtering, pulsed laser ablation, sol-gel techniques and metal organic chemical vapor deposition (MOCVD). For commercial device production, MOCVD is the preferred deposition technology. MOCVD provides for better coverage over topography than sputtering, and for greater production throughput than pulsed laser deposition or sol-gel techniques.

SBT, PZT and CMO belong to a general class of ceramic materials known as perovskites. Perovskites represent a technologically important class of materials with unique properties, such as ferroelectric, piezoelectric, electro-optic and superconducting properties. Thin films of perovskites are finding numerous applications in electronics, communications and power distribution. A production-worthy, low-temperature technology for deposition and processing of perovskite thin films will be beneficial for a wide variety of commercial applications.

EXPERIMENTAL DETAILS

The substrates used in this work were six inch diameter silicon wafers with a platinum electrode layer and a titania adhesion layer, over thermal oxide. The general substrate structure was Pt/TiO_2/SiO_2/Si(100). The SBT films were prepared by sol-gel technique, to a nominal thickness of 100 nm. All SBT films were pre-baked for 1 hour at 500 C, prior to either furnace annealing or laser annealing, in order to drive off any remaining volatiles from the sol-gel deposition process. The PZT and CMO films were prepared by MOCVD, in an SMI SpinCVD^{TM} rotating disk reactor. The nominal composition of the PZT films was $Pb(Zr_{0.3}Ti_{0.7})O_3$. Nominal thickness of the PZT and CMO films was 100 nm.

Excimer laser annealing was done using a Lambda Physik "Compex 102" KrF excimer laser, which has an output wavelength of 248 nm. All laser annealing was done in air and at room temperature. The laser pulse repetition rate was 10 Hz. We performed a systematic study of the laser pulse energy density (57.1, 105.2 and 127.3 mJ/cm^2) and total number of pulses (10, 100 and 1000) on the same wafer for each material investigated.

Furnace annealing of SBT films was done for comparison, and to provide baseline data for the laser annealing studies. All furnace anneals were done in a box furnace in air. The annealing process was 800 C for 60 minutes, followed by a furnace cool to below 500 C prior to removal to room temperature. Composition of the SBT films was determined by Electron Microprobe analysis using a Wavelength Dispersive X-ray Spectrometer. X-ray diffraction (XRD) was done to assess crystallinity and preferred orientation of all films before and after annealing. All XRD work was done on a Rigaku x-ray diffractometer, using Ni filtered Cu Kα radiation.

For selected SBT samples, capacitors were formed in the films to assess electrical properties and ferroelectric behavior. A thin gold film was evaporated through a shadow mask to form the upper capacitor electrode. The capacitor size was 100 micron by 100 micron. Current-voltage characterization was done to assess the quality of the dielectric layer, prior to the polarization versus electric field (P-E) measurements. The P-E behavior was determined by the Sawyer-Tower method, using a 1000 pF linear capacitor connected in series with the thin film capacitor. The frequency of the AC signal used for the P-E studies was 10 KHz.

RESULTS

Results of composition analysis for selected SBT films samples are shown in Table I. The results show the film composition was very close to the stoichiometric 1:2:2 target value, and was little affected by the annealing processes. In particular, no loss of bismuth was observed to occur during either furnace or laser annealing. Results of XRD analysis of the as-deposited and furnace annealed SBT thin films are shown in Figure 1. These results verify that the stoichiometric 1:2:2 phase crystallizes on furnace annealing at 800 C. Randomly oriented crystalline $SrBi_2Ta_2O_9$ is observed, as evident by the appearance of the (115), (200) and (135) diffraction peaks in Figure 1.

Table I: Composition of selected $SrBi_2Ta_2O_9$ films samples, before and after annealing.

Sample	Sr	Bi	Ta
As-Deposited	.85	2.11	2.04
Furnace Annealed 1 hr @ 800 C	.82	2.09	2.09
Laser Annealed 100 pulses @ 105.2 mJ/cm^2	.80	2.05	2.15

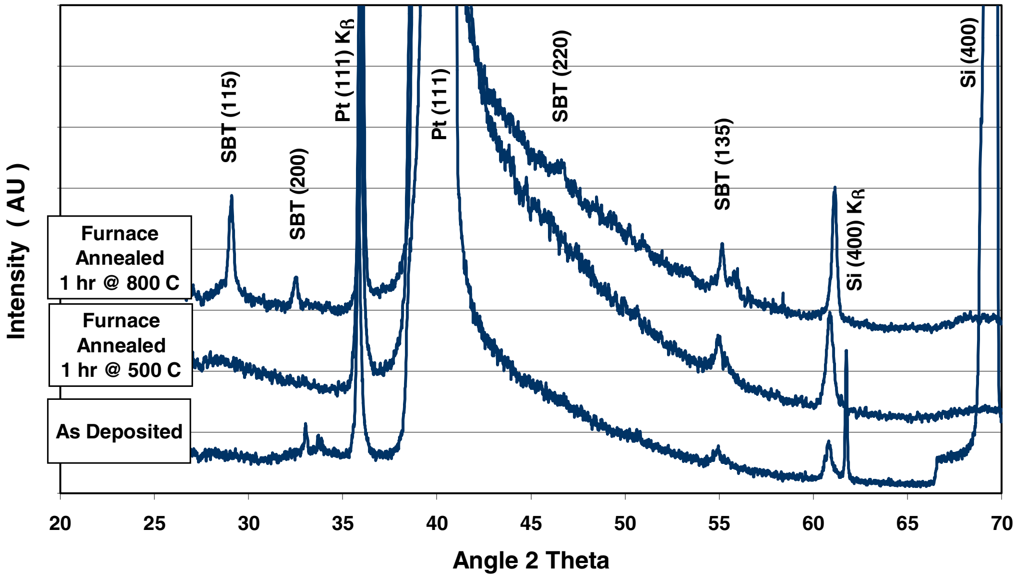

Figure 1: X-ray diffraction results for $SrBi_2Ta_2O_9$ films, in the as-deposited condition and after furnace annealing.

Figure 2 shows XRD results for SBT thin films which were laser annealed at an energy density of 105.2 mJ/cm^2. These results show that the stoichiometric 1:2:2 phase crystallizes on room temperature laser annealing with a strong (200) preferred orientation. SBT samples laser annealed at an energy density of 57.1 mJ/cm^2 showed essentially the same XRD results as the as-deposited material. For SBT films laser annealed at the highest energy density of

127.3 mJ/cm^2, we observed that considerable laser ablation had occurred. In some cases, the SBT film was completely removed from the substrate and the underlying materials exposed.

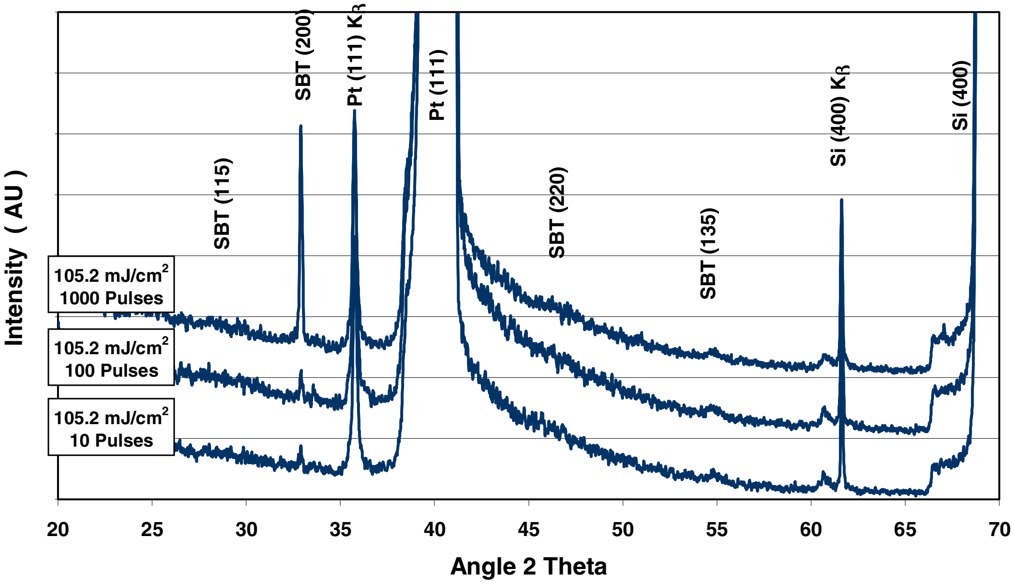

Figure 2: X-ray diffraction results for $SrBi_2Ta_2O_9$ thin films laser annealed at an energy density of 105.2 mJ/cm^2.

For the electrical characterization of the SBT films, we initially measured the current voltage characteristics, to determine the quality of the dielectric layer. We found leakage currents to be less than 10^{-6} amps for voltage scans from -6 V to + 6 V, for all $SrBi_2Ta_2O_9$ film samples. We next measured the polarization versus applied field (P-E) characteristics. We observed two distinct types of polarization behavior. Figure 3 shows a narrow elliptical polarization curve, which was typically observed for SBT films laser annealed at lower energy densities. These samples also showed no observable $SrBi_2Ta_2O_9$ peaks in the XRD spectra. Figure 4 shows P-E data for an SBT film laser annealed for 10 pulses at 105.2 mJ/cm^2. This curve shows pronounced hysteresis, with a remnant polarization ($2P_r$) of approximately 6 μC/cm^2. This sample contained crystalline $SrBi_2Ta_2O_9$ phase, as evidenced by x-ray diffraction. The results are consistent with the onset of crystallization and the onset of ferroelectric behavior for SBT films laser annealed at an energy density of 105.2 mJ/cm^2.

Figure 5 shows XRD results for MOCVD deposited PZT thin film samples, in the as-deposited condition and after laser annealing at 105.2 mJ/cm^2. This material was crystalline as deposited. We observed no increase in intensity of the diffraction peaks after laser annealing, for all PZT samples. Similar to the SBT material, we observed ablation of the film to occur on laser annealing at an energy density of 127.3 mJ/cm^2.

Similar experiments were conducted for cerium manganate thin films deposited by MOCVD at Structured Materials Industries. The CMO thin films were also crystalline as deposited. We observed no significant increase in intensity of the XRD peaks, after laser annealing of the $CeMnO_3$ film samples. Further work to characterize the electrical and ferroelectric properties of as-deposited and laser annealed PZT and CMO thin films is presently in progress. These results will be reported separately.

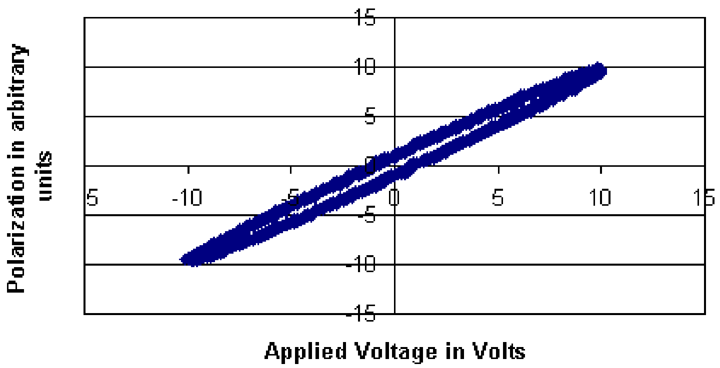

Figure 3: Polarization versus applied field for a $SrBi_2Ta_2O_9$ thin film after laser annealing 1000 pulses at 57.1 mJ/cm^2. The elliptical P-E curve indicates no ferroelectric behavior for this sample.

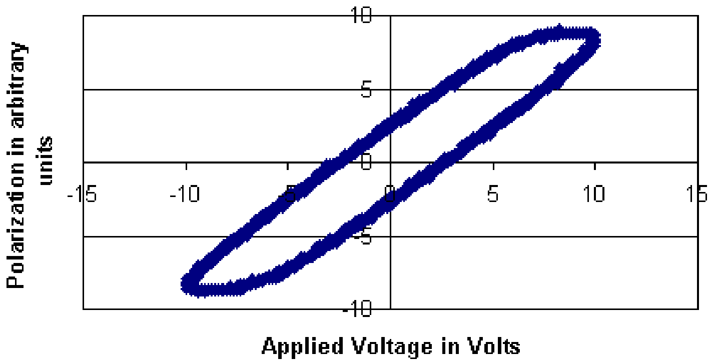

Figure 4: Polarization versus applied field for a $SrBi_2Ta_2O_9$ thin film after laser annealing 10 pulses at 105.2 mJ/cm^2. This data shows hysteresis in the P-E curve, indicating that at least some of the material has become ferroelectric.

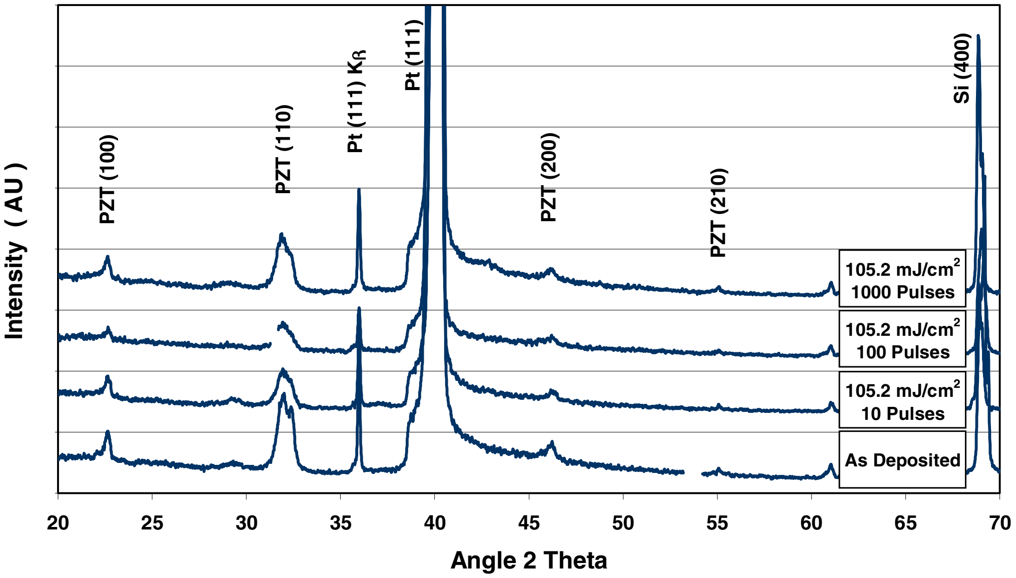

Figure 5: X-ray diffraction results for $Pb(Zr_xTi_{1-x})O_3$ thin films in the as-deposited condition and after laser annealing at an energy density of 105.2 mJ/cm^2.

CONCLUSIONS

We have investigated excimer laser annealing of sol-gel deposited SBT thin films and MOCVD deposited PZT and CMO thin films. For SBT, room temperature laser annealing crystallizes the stoichiometric $SrBi_2Ta_2O_9$ phase with a strong preferred (200) orientation, without exposing the substrate wafer to elevated temperature. The optimum laser energy density is approximately 105 mJ/cm^2. Lower laser energy density did not result in crystallization. Higher laser energy density resulted in ablation of the SBT film from the substrate. MOCVD deposited PZT and CMO thin films were crystalline as deposited. Laser annealing appeared to have little effect to induce further crystallization of either PZT or CMO, as evidenced by the intensities of the x-ray diffraction peaks. Similar to the SBT films samples, laser annealing at an energy density of 127.3 mJ/cm^2 resulted in laser ablation of the PZT film. Further electrical characterization of both PZT and CMO ferroelectric thin films is currently in progress at Structured Materials Industries and will be reported on separately.

Electrical characterization of the laser annealed SBT thin films show good dielectric behavior, with minimal leakage current. The films laser annealed at an energy density of 105.2 mJ/cm^2 show the onset of ferroelectric behavior, as indicated by hysteresis in the polarization versus applied field curves. The low temperature laser annealing process could enable integration of ferroelectric SBT films with silicon based micro-electronics, for ferroelectric memory applications.

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