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Metalorganic chemical vapor deposition of ferroelectric $SrBi_2Ta_2O_9$ thin films

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Ferroelectric layered-oxides $SrBi_2Ta_2O_9$ thin films were prepared on Pt coated Si wafers and single-crystal sapphire by metalorganic chemical vapor deposition (MOCVD). The films were specular and crack-free and showed complete crystallization at temperatures between 650 and 700 °C. Good ferroelectric properties were obtained for a 200 nm thick film with Pt electrodes: $2P_r$ and E_c were about 8.3 μC/cm^2 and 60 kV/cm, respectively. The leakage currents were as low as 8×10^{-9} A/cm^2 at 150 kV/cm. The films also showed fatigue-free characteristics: no fatigue was observed up to 1.4×10^{10} switching cycles. These high quality MOCVD films make high-intensity (>1 Mbit) nonvolatile memory devices possible. © *1996 American Institute of Physics.* [S0003-6951(96)00505-7]

In recent years, ferroelectric thin films have been integrated into silicon integrated circuits to provide high speed, high read/write endurance, high radiation hard, and low power consumption nonvolatile memory.[1] However, the densities of current commercially available ferroelectric random access memory (FRAM) devices are still low.[1] Although ferroelectric thin films have great potential for high-density (>Mbit) FRAMs, commercial usage has been hindered largely by serious degradation problems such as fatigue, imprint, retention, and aging that reduce the devices's lifetime.[2] Since polarization must be reversed to read or write data in a memory cell, fatigue is a critical obstacle for practical use.

The most popular ferroelectric materials under investigations for nonvolatile memory applications are $PbZr_xTi_{1-x}O_3$ (PZT) because they have a high Curie temperature, large remanent polarization, and well-known properties. However, these ferroelectric capacitors have serious fatigue degradation problems after about 10^8 read/write cycles that are not enough for intensive read/write applications. Several models can be found in the literature to explain the individual degradation mechanisms. Recently, Desu and Yoo[3] have proposed a unified model in which oxygen vacancies are cited as the common source for most degradation phenomena. The model suggests two possible solutions to overcome fatigue: reducing entrapments by changing the nature of the electrode/ferroelectric interface and controlling defect density of the ferroelectrics. Paz de Araujo, etc.[4] indicated that fatigue also came from another different microscopic cause: stress relaxation of 90° domains in pseudocubic crystals (such as lead zirconate titanate family). The 90° domain is more likely to be pinned than the 180° domain. For this reason, reducing the 90° domain may improve fatigue properties. Research has been conducted to improve the fatigue properties of PZT capacitors by using conductive oxide electrodes such as $La_xSr_{1-x}CoO_3$ and RuO_2 or by doping La or Nb into the films.[5–8] However, its disadvantage is that the resulting device is electrically ''leaky,'' with dc leakage currents that may be too high for some nonvolatile memory device and for dynamic random access memories (DRAMSs).[9,10] An alternative approach is to find new ferroelectric materials with low intrinsic defect density such as $SrBi_2Ta_2O_9$ (SBT) which are known as layered oxides.

Recently, SBT films were successfully prepared by several research groups[11–17] using metalorganic decomposition (MOD)[11–15] or pulsed laser deposition (PLD)[16,17] techniques. All the reported data on these materials showed very attractive ferroelectric properties and fatigue-free characteristics. However, neither MOD nor PLD are suitable for high density device applications due to their poor step coverage. In this letter, we present the structural, optical, and ferroelectric properties of MOCVD SBT films.

The SBN films were prepared on $Pt/Ti/SiO_2/Si$ substrates and sapphire disks by metalorganic chemical vapor deposition. The typical process conditions are shown in Table I. The bis(2,2,6,6-tetramethyl-3,5-heptanedionato) strontium hydrate $[Sr(TMHD)_2]$, triphenylbismuth

TABLE I. Typical growth conditions of MOCVD $SrBi_2Ta_2O_9$ films.

Deposition pressure	4–10 Torr
Substrate temperature	500–650 °C
N_2 flow rate	500 sccm
O_2 flow rate	800 sccm
Liquid source flow rate	0.1–0.5 ml/min
Deposition time	60–90 min

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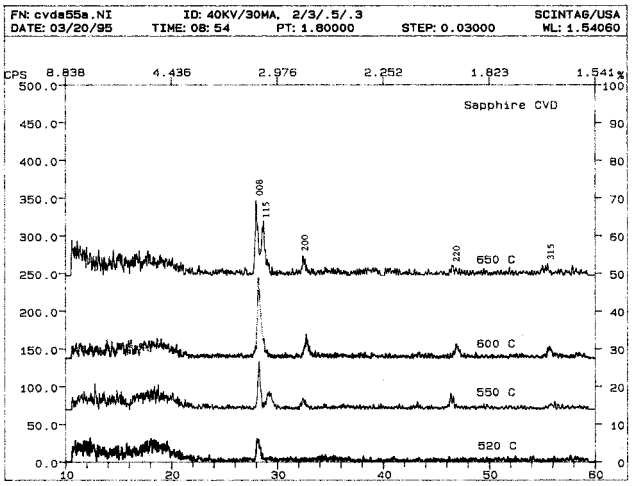

FIG. 1. XRD patterns of as-deposited MOCVD $SrBi_2Ta_2O_9$ films on sapphire at various deposition temperatures.

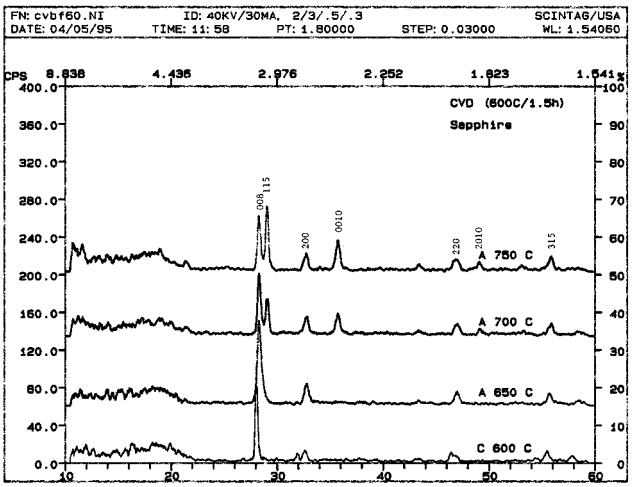

FIG. 2. XRD patterns of MOCVD $SrBi_2Ta_2O_9$ films on sapphire. The films were deposited at 600 °C and annealed at various temperatures.

$[Bi(C_6H_5)_3]$, tantalum ethoxide $[Ta(OC_2H_5)_5]$ were used as starting materials with a mixture of tetrahydrofuran, isopropanol, and tetraglyme in the molar ratio of 8:2:1 as the solvent. The organic precursors were mixed, and dissolved in solvent to form source solution with concentration of 0.1–0.5 M/L of SBT. The source solution was injected into the heated vaporization chamber to form precursor gases by a liquid pump. Smooth and specular SBT films were obtained. The thickness of SBN films were about 200 nm. The phases of the film were identified using x-ray diffraction (XRD). The surface morphologies of the films were characterized by scanning electron microscopy (SEM). The optical properties of SBT films on $Pt/Ti/SiO_2/Si$ substrates were measured by both UV-Vis-NIR spectrophotometry and variable angle spectroscopic ellipsometry. The ferroelectric properties were measured using a standardized RT66A tester. The top electrodes used were sputtered platinum using a shadow mask. The area of the top electrode was 2.1×10^{-4} cm^2.

The films were deposited at temperatures ranging from 500 to 650 °C. As-deposited films were specular, crack-free, uniform, and adhered well on the substrates used and were highly transparent on sapphire substrates. These films also showed very smooth surfaces as viewed by means of both optical microscopy and scanning electron microscopy. The film growth rates were typically in the range of 3–5 nm/min.

Figure 1 shows the x-ray diffraction (XRD) patterns of the as-deposited SBT films on sapphire substrates as a function of deposition temperature. Only small x-ray peaks were observed when the films were deposited at 550 °C or lower. The major XRD peaks corresponding to (115) and (200) planes were observed when the films were deposited at 600 °C. At a deposition temperature of 650 °C, the films showed well-crystalline feature as can be seen in the figure. Figure 2 shows the XRD patterns of the 600 °C deposited MOCVD SBT films on sapphire as a function of postdeposition annealing temperature. As expected, at an annealing temperature of 700 °C, sharp and numerous XRD peaks were observed, which indicated very well-crystallized films. For the surface morphology, the films appeared uniformly distributed fine grains and crack-free under SEM examinations. The SEM micrograph of the surface of annealed film is shown in Fig. 3. The average grain size is around 100 nm. The refractive index of the films was around 2.3 measured by variable angle spectroscopic ellipsometry. This value is very close to that of 98% dense polycrystalline bulk SBT samples,[18] which indicates a highly dense film.

The hysteresis loops of the MOCVD SBT films annealed at 750 °C are shown in Fig. 4. The thickness of the film was around 200 nm. As can be seen in the figure, the loops were saturated at 3 V. The remanent polarization $(2P_r)$ and the coercive field (E_c) of SBT films were 8.3 $\mu C/cm^2$ and 60 kV/cm at an applied voltage of 5 V, respectively. Figure 5 shows fatigue characteristics of the film. The film was pulsed at 5 V of 1 MHz bipolar square wave. The film did not show any fatigue after the sample was switched up to 1.4×10^{10} cycles. Furthermore, no noticeable change on the hysteresis loops before and after the fatigue test was observed. It is believed that the superior fatigue properties of the SBT films are due to the Bi-layered structure. Unlike PZT, the thermal stability of the SBT compound is up to 1150 °C.[19] Because the process temperature of SBT is below 800 °C, there are no

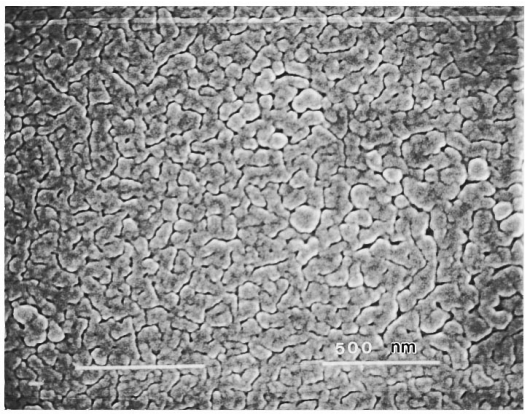

FIG. 3. SEM surface morphology of MOCVD $SrBi_2Ta_2O_9$ films on Pt-coated Si substrates.

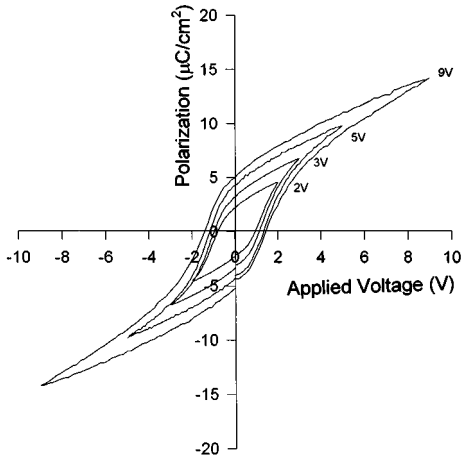

FIG. 4. Hysteresis loops of MOCVD $SrBi_2Ta_2O_9$ films on Pt-coated Si substrates. The film thickness is around 200 nm.

volatile species that result in defects at process temperature. On the other hand, Bi-layer oxides have large polarization along the *a* or *b* axis, but little or no polarization along the *c* axis, thus most of the domain configuration in Bi-layer oxides is the 180° domain.[8] For this reason, the BST has excellent fatigue properties.

Low leakage current density is another important consideration for memory device applications. Figure 6 shows the *I–V* curve of a 200 nm thick MOCVD SBT films annealed at 750 °C. Excellent *I–V* characteristics were observed. The leakage current density at 150 kV/cm was around 8.4×10^{-9} A/cm^2. There is a significant difference in the measured room-temperature leakage current density values of the MOCVD films and the reported values for the laser ablated films.[16] Under the same conditions of the applied electric field, the MOCVD derived films display leakage current densities at least an order of magnitude lower than the corresponding laser ablated films. Although further investigation is needed to identify the cause of this difference, one possible factor could be the smaller grain size and higher density of MOCVD films.

In summary, ferroelectric $SrBi_2Ta_2O_9$ thin films were reproducibly fabricated on $Pt/Ti/SiO_2/Si$ and sapphire substrates by the MOCVD technique. The films showed superior optical, ferroelectric, and fatigue properties which meet the requirements for high-density nonvolatile memory device applications. The optimization of the deposition parameters is currently under investigation.

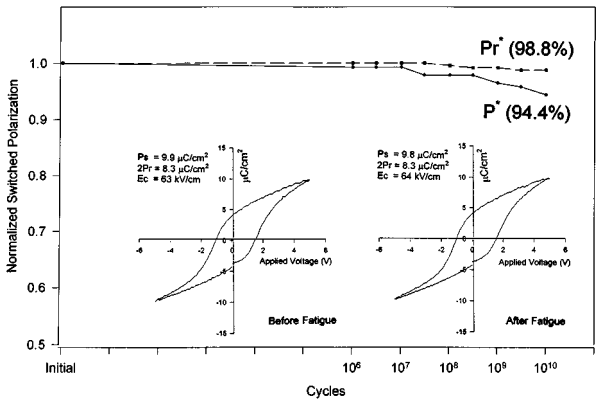

FIG. 5. Fatigue curves of MOCVD $SrBi_2Ta_2O_9$ films on Pt-coated Si substrates. The hysteresis loops before and after fatigue test are also shown.

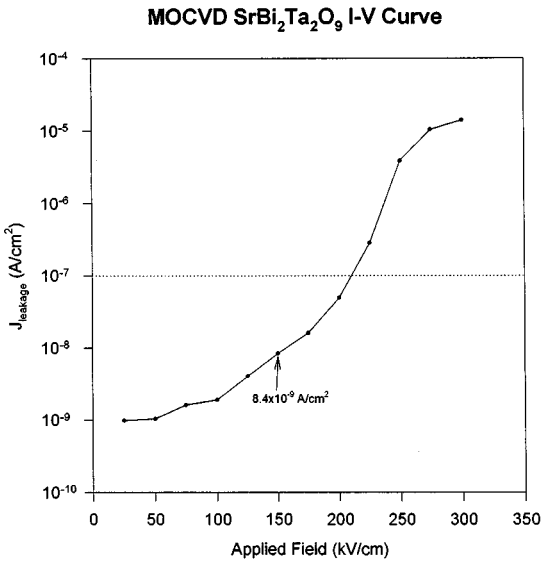

FIG. 6. Leakage current of MOCVD $SrBi_2Ta_2O_9$ films on Pt-coated Si substrates.

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