FRONTIERS in SCIENCE and TECHNOLOGY

Ferroelectrics

Vol. 1

V. Stefan
Editor-in-Chief

The STEFAN UNIVERSITY Press
Series on Frontiers in
Science and Technology

FRONTIERS in SCIENCE and TECHNOLOGY

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NEW TECHNOLOGIES FOR FUTURE FeRAMs

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NEW TECHNOLOGIES FOR FUTURE FeRAMs in:
V. Stefan (Editor-in-Chief) . FERROELECTRICS. Vol. 1.
(*The Stefan University Press Series on Frontiers in Science and Technology, ISSN; 1543-4028. La Jolla, CA. 2002.*)
pp. 125-134.
ISBN: 1889545287

1. Introduction

$SrBi_2Ta_2O_9$ (SBT) is a promising material for ferroelectric non-volatile memories (FeRAMs) because of its fatigue free nature[1]. At present, crystallization techniques, such as metal organic decomposition (MOD) etc., are commonly used for SBT film fabrication. These techniques usually require processing temperatures higher than 750°C for crystallization at thermal equilibrium to achieve good electrical properties. However, these high processing temperatures do not meet high-density CMOS LSIs with salicide contacts. Thus the lowering of processing temperature is a crucial requirement for future FeRAMs of 4M bit or higher.

To lower the processing temperature, we took two different approaches. One is the modification of conventional techniques by optimizing process conditions and the other is the use of metal organic chemical vapor deposition (MOCVD) that can control ferroelectric crystallinities by depositing films under quasi-epitaxial growth conditions.

In addition, MOCVD can also achieve conformal depositions onto the stepped electrodes with high aspect ratios. In this reason, MOCVD is considered to be the most suitable deposition technique for high density FeRAMs. However, several problems to be solved are existed in the ferroelectric MOCVDs. These problems are brought to be the low vapor pressure of the MO precursors, especially Sr sources. To solve this problem, we have proposed new MO delivery system.

In this paper, we will demonstrate excellent electrical properties of SBT prepared at temperatures lower than 700°C and discuss possibilities of further lowering of the processing temperature for future high-density FeRAMs. In addition, we will describe the features of our MOCVD machine that are suitable for mass production use.

2. New Fabrication Techniques of the Ferroelectrics for future FeRAMs

I. Low temperature processing -Modification of conventional techniques

As an extension of existing deposition techniques, we tried to lower the processing temperature through the refinement of those deposition conditions. The optimized conditions include starting chemicals, gas flow rates in a furnace, thermal treatment conditions, etc.

Figure 1 is the schematic diagram of the free energy in SBT system. In this SBT system, a fluorite phase is existed in the low temperature range and the perovskite phase, which is possess ferroelectric properties, is considered to be high temperature phase. Even at 650°C perovskite is stable, however, the free energy is close to that of the fluorite. Thus, the fluorite phase might be remained as a quasi-equilibrium state at. 650°C

The fluorite phase would be generated during heating up to 650°C and it takes more than several hours to transform from fluorite to perovskite at as low as 650°C. However, this phase transformation is easily affected by ferro-annealing conditions, the optimization of the deposition conditions, such as gas flow rate etc., can enhance this phase transformation.

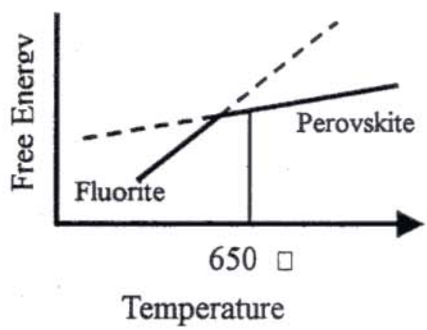

Figure 1 Schematic diagram of the free energy in the SBT system.

Figure 2 shows the XRD profiles of the samples that are ferro-annealed at 650°C for 1 hour. Both samples are fabricated by LSMCD using a same starting chemical. The sample fabricated using conventional conditions, which is used in our present development, shows a single fluorite phase. In turn, the samples optimized for the 650°C processing shows a single perovskite phase. This result suggests optimizing the process conditions bring the 650 processing even in the conventional procedures.

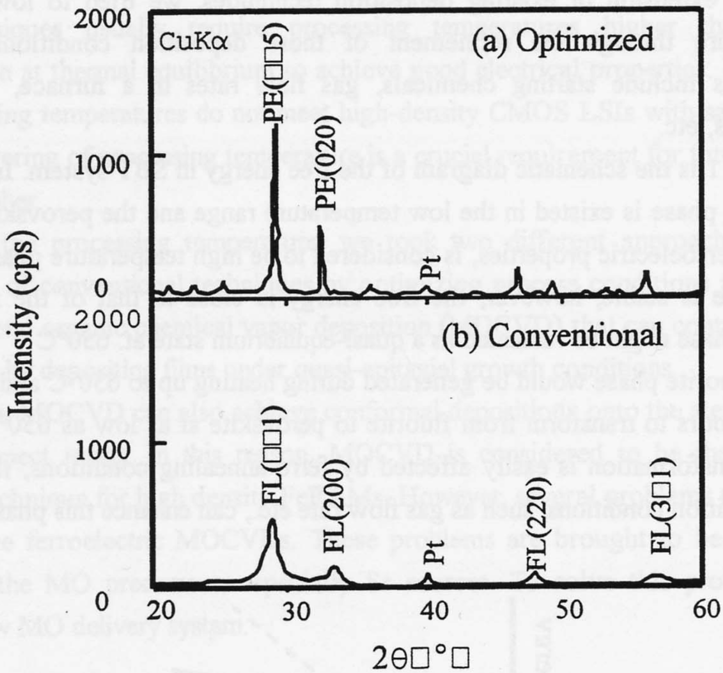

Figure 2 The X-ray diffraction profile of the samples that are fabricated at 650°C process. Ferro-annealing conditions are 650°C for 1hour in the oxygen. The sample (a) is fabricated in the optimized conditions. In turn, the sample (b) is fabricated in the conventional conditions that are used in the 800°C process.

The other approach for the low temperature processing is the modification of the present processes. For example, the use of sol-gel based chemicals as starting materials can lower the process temperature[2]-[4]. As shown in fig. 3, the sol-gel-based chemicals involve ion networks those are similar to that of SBT ferroelectrics[2]-[4]. These networks will enhance the crystallization from the starting chemicals into the SBT ferroelectrics, which results in the lowering the process temperatures.

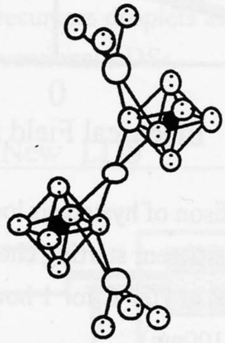

Figure 3 Schematic diagram of the ion-networks in the sol-gel-based chemicals. The networks in this chemicals are similar to those of the SBT perovskite.

As an example, a comparison of hysteresis loops for SBT samples fabricated from different starting chemicals are given in fig. 4. Both of the samples were prepared at a temperature of 700°C. The conventional chemical used is a MOD solution. On the other hand, the new one is based on a sol-gel solution that involves the ion-networking. These networks are the similar to that of SBT

As shown in fig. 4, the use of this new chemical has provided an improved remnant polarization with a superior shape of the hysteresis loop even at 700°C. This result suggests that the refinements of the starting chemicals have a potential for lowering the process temperature.

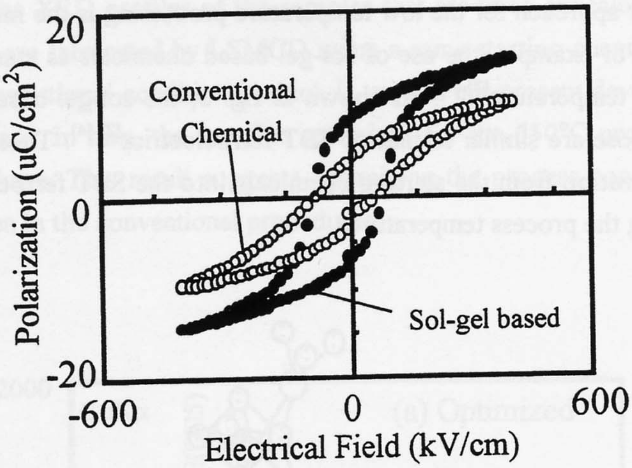

Figure 4 Comparison of hysteresis loops of the samples fabricated using different starting chemicals. Both samples are ferro-annealed at 700°C for 1 hour.
(Film thickness: 100nm)

As mentioned in this section, we can conclude that the lowering a process temperature less than 650°C is a realizable specification of SBT. This means that the SBT is also applicable for the high-density FeRAMs. We have been investigating further improvements of these methods for mass-production.

II. New deposition technique-MOCVD

MOCVD is a deposition technique wildly used in the compound semiconductor production and can achieve good conformal films onto the high aspect ratio steps. Based on the similar consideration, a ferroelectric MOCVD technique has also been developed in these few years for DRAM and FeRAM applications.

However, this ferroelectric MOCVD technique has one big problem to be solved for the mass-production. As the vapor pressures used in ferroelectric MOCVD are extremely low, the use of the conventional gas delivery system, i.e. bubbler system, results in low reproducibility and low deposition rates. In order to solve this issue, liquid-source delivery systems (LDSs) have been commonly employed for ferroelectric MOCVD. In spite of the use of the LDSs, clogging of precursors in the vaporizer still occurs and, therefore, further improvements are necessary.

In these years, we have been developed a new LDS based on a new idea to solve this problem[5]. Figure 5 represents a schematic diagram of our system. The most specific feature of this system is the use of an atomizer with a vaporizer. This atomizer is generates a small droplet of the precursor as a mist to be transferred into the vaporizer. The atomizer of our LDS can generate the precursors droplets as small as 0.3 μm, which is much smaller than those generated in the conventional LDSs.

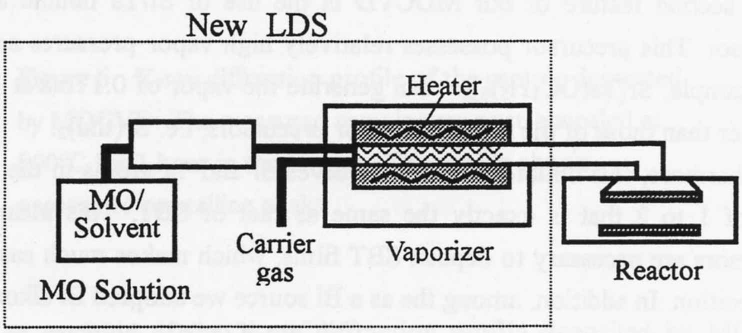

Figure 5 Schematic diagram of new LDS system. This LDS is based on the idea of atomizer /vaporizer system, which is enhance the vaporization efficiency of the MO precursors.

As shown in table 1, the ratio of the surface area and the volume of droplets, the S/V ratio (where S is the surface area and V is the volume), is inversely proportional to its size. Thus, the smaller droplet, i.e., misted precursor, has a large S/V ratio. This system promotes fast precursor vaporization due to the larger S/V ratio. This means that we can deliver much larger amount of the precursors, which means the deposition rate has been dramatically improved.

Table 1 Example of the specific surface are for liquid weighing 1 gram (assuming unit density) The new LDS shows efficient heating due to high surface area of mist particles

Mist size	Specific Area
10 μm diameter	6,000 cm^2
1 μm diameter	60,000 cm^2
0.1 μm diameter	600,000 cm^2

The second feature of our MOCVD is the use of Sr/Ta double alkoxide as a Sr/ Ta precursor. This precursor possesses relatively high vapor pressures among the Sr sources. For example, $Sr[Ta(OC_2H_5)_6]_2$ can generate the vapor of 0.1Torr at 170°C and this value is higher than those of the conventional Sr precursors, i.e. $Sr(thd)_2$.

Furthermore, this double alkoxide involves Sr and Ta atoms in the one molecule with a ratio of 1 to 2 that is exactly the same as that of SBT. This means that the only two precursors are necessary to deposit SBT films, which makes much easier to adjust the SBT composition. In addition, among the as a Bi source we adopted Bi alkoxide.

Our deposition conditions are summarized in Table 2.

Table 2 The fabrication conditions of SBT-MOCVD

MO Precursors	$Sr[Ta(OC_2H_5)_6]_2$ /THF $Bi(OC_5H_{11})_3$/THF
Depo. Temp	400□□700□
Film Thickness	100□200nm
Cap. structure	Pt/SBT/Pt
Post-annealing	400□□800□ in O_2, 1hour

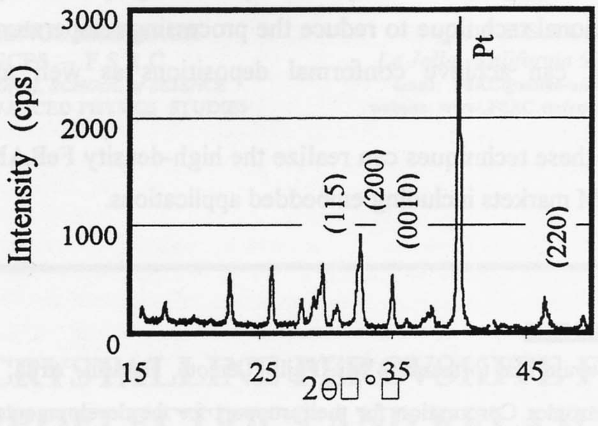

Figure 6 X-ray diffraction profile of the sample deposited by MOCVD. The measured sample was post-annealed at 800°C for 1 hour in the oxygen. The profile shows perovskite crystalline peaks.

Figure 6 is an example of the X-ray diffraction profile deposited by MOCVD. The measured sample was post-annealed at 800°C for 1 hour and shows perovskite crystalline peaks. As this sample requires a high temperature post-annealing, we have been developing the lowering this process temperatures.

However, no clogging problem was observed in this MOCVD system during a series of the experiments. This suggests the excellent performance of the new LDS system that are applicable for mass-production.

Based on this new LDS, we are investigating ferroelectric MOCVD techniques to achieve an excellent conformal film and a low temperature processing at 650°C for sub-quarter micron LSI applications.

3. Summary

We are approaching the low temperature processing by two ways. One is a modification of the conventional technique to reduce the processing temperature. Another is a MOCVD technique that can achieve conformal depositions as well as lowering the process temperature.

We believe these techniques can realize the high-density FeRAMs in the near future and enlarge FeRAM markets including embedded applications.

Acknowledgements

The authors would like to thank to Mr. Fujii, Uemoto, Hayashi, Arita, Noma, Nasu and Tanaka of Matsushita Electronics Corporation for their support for the developments. The authors also thank to Mr. McMillan of Symetrix for his kind encouragement.

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