Extended Abstracts of the 1991 International Conference on Solid State Devices and Materials, Yokohama, 1991, pp. 195-197

Single-Target Sputtering Process for PZT Thin Films with Precise Composition Control

Kazuyoshi Torii, Toru Kaga, Keiko Kushida, Hiroshi Takeuchi, and Eiji Takeda

Central Research Lab., Hitachi Ltd.

Kokubunji, Tokyo 185 JAPAN

The influence of growth conditions on rf-magnetron sputtered lead zirconate titanate (or PZT) thin films has been investigated, and the structural and electrical properties of PZT thin films have been examined.

It was found that the Pb content in a sputtered film is proportional to rf power, thereby making it possible to control the film composition precisely. A well-crystallized structure was obtained by post-deposition annealing at 590°C. A film with a proper Pb content (i.e., Pb/Zr+Ti=1) has the dielectric constant of 1180.

1. Introduction

The large charge density requirement for the future generations of DRAMs has generated a strong demand for alternative dielectrics.

Lead zirconate titanate ($Pb(Zr,Ti)O_3$,or PZT) and its family are very attractive for DRAM applications in light of their high dielectric constant. If we can make thin films of the PZT family whose dielectric constant is larger than 1000, and whose thickness is less than 250Å, giga-bit DRAMs can be achieved by a simple memory cell structure.

Single-target sputtering method is likely to be a dominant growth technique for PZT thin films because the simplest process meeting the device fabrication requirements is the most desirable. However, it is said that this method has disadvantages such as compositional changes in the film from the target, low deposition rate, and generation of surface damages.[1] We have succeeded in solving these problems and establishing a single-target magnetron sputtering process for PZT thin films with precise composition control. We also found that Pb content in a PZT film strongly affects its electrical properties.

2. Film preparation

PZT thin films were prepared on $Pt/SiO_2/Si$ substrates by rf-magnetron sputtering method. On a 1000Å thick thermal oxidation SiO_2, a [111] oriented Pt thin film, whose thickness was 1000Å was deposited as a lower electrode by DC sputtering.

The sputtering target was a PZT ceramics in which excess PbO of 15 mol% was added to compensate for the loss of Pb from the sputtered films. The concentration of the target was examined by ICP-AES (Inductively Coupled argon Plasma Atomic Emission Spectrometry), and Zr/Ti ratio was found to be 49.7/50.3.

Gold electrodes with a diameter of 200μm were evaporated on the PZT films to measure the electrical properties.

3. Composition Control

The control of the film composition is very important because the electric properties of a PZT thin film is drastically change with its composition.

The chemical composition of the PZT films were determined by ICP-AES. The Pb content of the films was found to change with sputtering gas pressure as shown in Fig. 1. On the other hand, the Zr/Ti ratio values of the films were almost equal to that of the target irrespective of the sputtering gas pressure.

Sputtered at a lower gas pressure, the Pb content in a sputtered film is less than that of the target; it approaches the target composition as the pressure is increased. This compositional change is supposed to be caused by preferential re-sputtering by accelerated negative ions.

Many previous works have dealt with sputtering gas pressure less than 5 Pa to obtain a high deposition rate.[2-4] However, we need not consider the deposition rate for memory applications, because very thin PZT films are required. In our experiments, the films with the desired composition were obtained around 15 Pa. At pressure values as high as 15 Pa, the mean free path of sputtered atoms and ions was in the order of millimeters

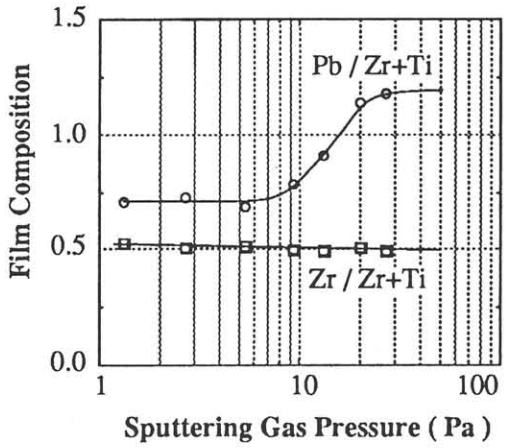


Fig. 1 Sputter Gas Pressure dependence of Film Composition

and the impingement of high energy ions was reduced. Thus compositional changes and damages which were also caused by high energy ions were suppressed.

Figure 2 shows the rf power dependence of film composition. The Pb content in the films decreases in proportion to the rf power. The Zr/Ti ratio of the films changes only slightly. This compositional change with rf power may also be caused by selective resputtering of Pb from the films by the high energy negative ions.

Because the compositional change is proportional to the rf power and the rf power can be controlled easily and precisely compared with the other sputtering parameters, we can adjust the film composition exactly by the rf power.

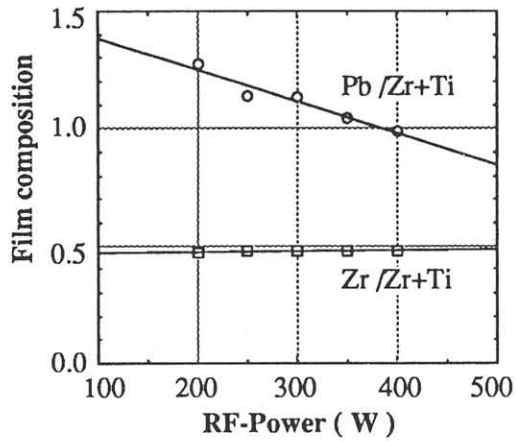


Fig. 2 RF power dependence of film composition

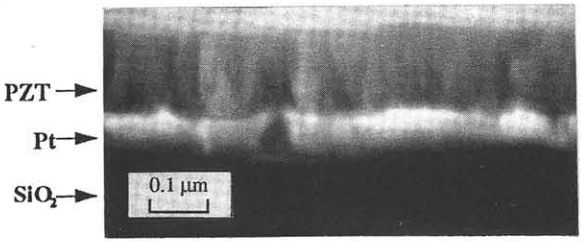


Fig. 4 Scanning electron micrograph of annealed film

4. Crystallographic Structure

For a film sputtered at 200°C substrate temperature, post-deposition annealing was required to achieve a well crystallized perovskite structure. In situ observations were made by X-ray diffraction (XRD) using a small furnace which can be set on a conventional goniometer, in order to examine the structural change of the films during post-deposition annealing.

As shown in Fig. 3 (b), the first structural transformation occurred at 480°C. Four peaks observed for the as-grown film started to disappear and a new peak at 33.5° began to appear. Between 480°C to 580°C, this peak grew and sharpened.

The second structural transformation occurred at 590°C (Fig. 3 (d)). Peaks corresponding to the perovskite structure appeared. This transformation was much faster than the first one. The peak width was very sharp when it appeared, and it changed very little even after a long annealing. In the giga-bit generation, interconnections formed after bit line may be made of refractory metals such as tungsten. Since the ferroelectric thin film is made after bit lines formation in the simple STC cell, it must be formed at less than 600 °C for fear of reacting tungsten on silicon. The crystallization temperature of 590°C meets this requirement. PZT films sputtered at 200°C were annealed at 600°C for 2 hours for electrical property measurements. A film sputtered at 600°C substrate temperature also had the perovskite structure. As can be seen in cross sectional SEM micrograph in Fig. 4, annealed films have a clear columnar structure.

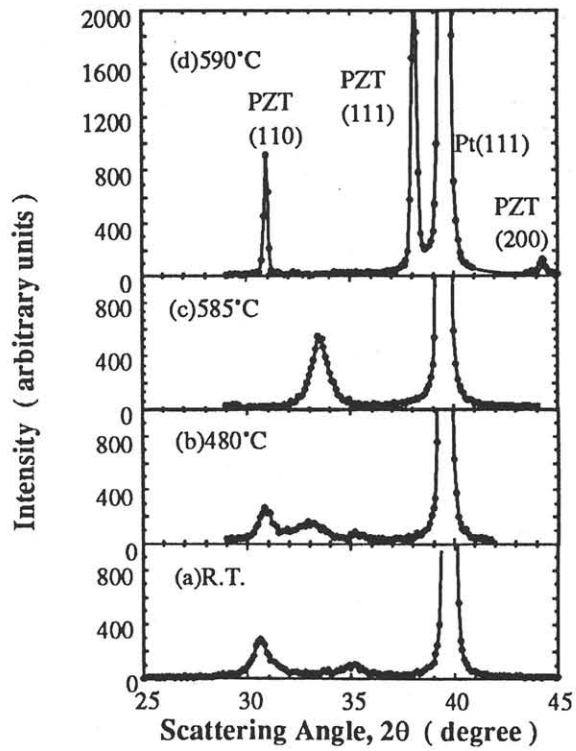


Fig. 3 Structural change of a film during post-deposition annealing (XRD profiles)

5. Electrical properties

The electric properties of annealed films were measured as a function of film composition. Dielectric constant and resistivity depend strongly on film composition as shown in Fig. 5. The highest value of dielectric constant value ε=1180 was found in the film whose Pb content was such that the ratio Pb/Zr+Ti was 1.

A small peak at 29.8° was observed by XRD for the films whose Pb content ratio Pb/Zr+Ti was less then 1. Thus these films have a small amount of second phase. This second phase must have caused the dielectric constant decreace. On the other hand, the films with excess Pb atoms appeared to be single phase by XRD measurement. The crystalline orientation of the PZT film with Pb/Zr+Ti>1 changed with film composition. The more excess Pb atoms were contained, the more the film (111) oriented. This change in crystalline orientation with Pb content may affect the electrical properties of PZT films.

D-E hysteresis loops were observed by a Sawyer- Tower circuit with 1 kHz sine wave (Fig. 6). The remanent polarization P_r of 22.5 μC/cm² and coercive field E_c of 52 kV/cm were obtained for the PZT film with composition of Pb/Zr+Ti=1.02. These values are the same as the bulk PZT's.

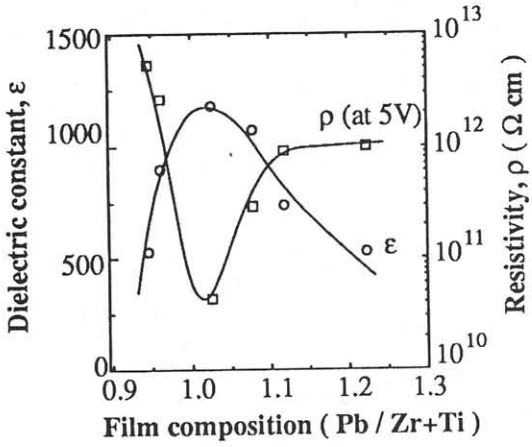
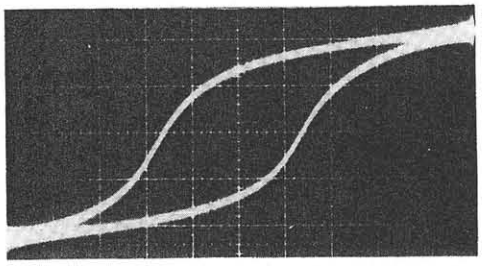


Fig. 5 Film composition dependence of dielectric constant and resistivity



Vertical scale : 10.5 μC /cm² / div
Horizontal scale : 67 kV / cm / div

Fig. 6 D-E hysteresis loop of an annealed film. (The film thickness was 1.5 μm, ε=1080)

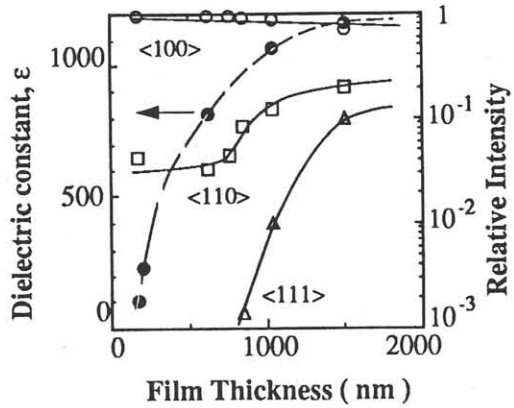


Fig. 7 Film thickness dependence of dielectric constant and crystalline orientation

Dielectric constant falls with decreasing film thickness. This phenomena of falling dielectric constant with decreasing film thickness was also reported ,[5,6] and is the most pressing problem for DRAM application. The crystalline structure of the film was found to be changed from polycrystalline one to (100) oriented one with decreasing film thickness as shown in Fig. 7, and this crystalline orientation change related to the fall in dielectric constant.

6. Conclusions

Precise composition control in single-target sputtering for PZT thin film was achieved by high pressure sputtering and by rf power control. From the in situ observations during post annealing , crystallization was found to occur at 590°C ; this is compatible with gigabit a DRAM process. An annealed film having a proper quantity of Pb has a dielectric constant (ε=1180) as large as that of bulk PZT.

Acknowledgement

The authors are grateful to Prof. N.Wakabayashi for his helpful discussions on the crystallographic structure and its change for the PZT films. They also gratefully acknowledge the managerial support of from Dr. K. Shimohigashi.

Reference

1. T.Nakagawa et al., Jpn. J. Appl. Phys. 21, L655-656 (1982)
2. R.Takayama and Y.Tomita, J.Appl.Phys. 65, pp.1666-1670 (1989)
3. A.Okada , J.Appl.Phys. 48, pp.2905-2909 (1977)
4. K.Sreenivas and M.Sayer, J. Appl. Phys. 64, pp.1484-1493 (1988)
5. H.Hamada et al., Oyo Buturi, 48, pp.602-608 (1979)
6. K.Sreenivas and M.Sayer J. Appl. Phys. 64, pp.1484-1493 (1988)