Structural Investigations of RuO_2 and Pt Films for the Applications of Memory Devices.

S. M. Jung, Y. S. Choi, D. G. Lim, Y. Park, and J. Yi.

School of Electrical and Engineering, SungKyunKwan University
300 Chunchun-dong, Jangan-gu, Suwon, Kyunggi-do 440-746(Korea)

Abstract

Lead zirconate titanate (PZT) is an attractive material for the memory device applications. We have investigated Pt and RuO_2 as a bottom electrode for a device application of PZT thin film. The bottom electrodes were prepared by using an RF magnetron sputtering method. The substrate temperature influenced the resistivity of Pt and RuO_2 as well as the film crystal structure. XRD examination shows that a preferred (111) orientations for the substrate temperature of 300°C. From the XRD and AFM results, we recommend the substrate temperature of 300°C for the bottom electrode growth. We investigated an anneal temperature effect because Perovskite PZT structure is recommended for the memory device applications and the structural transformation is occurred only after an elevated heat treatment. As post anneal temperature was increased from RT to 700°C, the resistivity of Pt and RuO_2 was decreased. Surface morphology was observed by AFM as a function of post anneal temperature.

1. Introduction

In recent years, ferroelectric materials have been investigated for applications of integrated memory devices. For the development of Gigabit dynamic random access memory(DRAM) device, high dielectric constant materials are required to obtain a proper charge storage in a reduced cell area. To realize the integration between the high performance ferroelectric capacitor and the active devices sitting on the semiconductor wafer, undesirable interactions between ferroelectric and semiconductor must be avoided. Any interaction at the interface not only degrades the performance of the capacitor, but also changes the characteristics of the underlying devices located on the semiconductor substrates. The electrode material should not chemically interact with the ferroelectric material nor form a low permittivity compound at the interface. It must also be stable enough at an elevated processing temperature. For this purpose, we investigated experimental research work on Pt and RuO_2 as a bottom electrode of ferroelectric thin film capacitor. In ferroelectric capacitor application, Pt electrode show a low resistivity and capacitor leakage current. RuO_2 electrode has a good fatigue behavior, thermal stability, and easy of etching.

2. Experimental

Prior to the deposition of bottom electrodes, oxidized p-type Si (100) substrates were cleaned in acetone, methanol, and deionized water. Promptly loading the prepared samples, we created a base pressure less than 5×10^{-6}torr prior to the thin film growth. The Pt thin film was deposited using RF magnetron sputtering from a Pt target with purity of 99.999%. The substrate and target were separated by a distance about 6cm. The gas pressure of Ar and O_2 were maintained at about 7mTorr. Input power was ranged from 40W to 80W with substrate temperature variation from RT to 300°C. The RuO_2 thin film was sputtered from a Ru target distance of 7cm with purity of 99.999%. The modulation of gas flow rate was carried out to form either RuO_2 or Ru thin film. For RuO_2 film growth, we varied the substrate temperature from RT to 400°C. Because a ferroelectric films are formed at temperature higher than 550°C, we investigated post anneal temperature effect on bottom electrode. An electrical property was investigated by four points probe system (Signatone S-30L system). The surface morphology and crystallographic properties of the films deposited at different substrate temperature were characterized by AFM (Mitutoyo Auto-probe CP) and XRD (Mac Science M18XHF-SRA).

3. Result and discussion

Thin film growth rate was investigated in terms of RF power, gas pressure of O_2 and Ar. substrate temperature. The growth rate exhibited a linear increase from 190 Å/min. at 40W to 390Å/min. for 80W. Pt films exhibited peak intensity of (111) as shown in Fig. 1 for the various RF power and substrate temperatures. RF power dependence was small for the low and high substrate temperature because of the surface energy was either too low or high for a suitable crystalline film growth. The substrate temperature of 200°C exhibited strong dependance on input power. As the power increases linearly, so does the (111) peak intensity. The crystallinity of Pt film was strongly influenced by the substrate temperature. Room temperature grown films showed small grain size and post anneal treatment higher than 300°C achieved a well-crystallized structure as can be seen in Tab. 1.

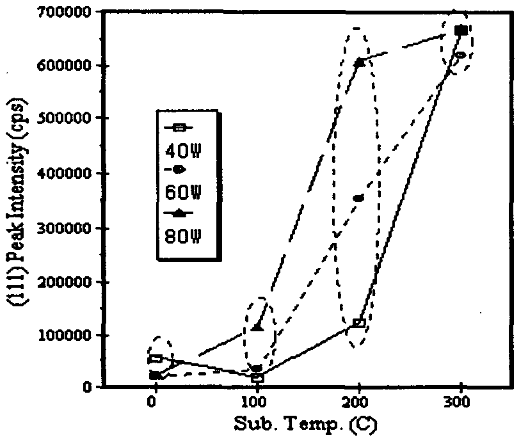

Fig 1. Peak intensity of (111) plane for Pt thin film as a function of substrate temperature and RF input power.

Table 1. AFM Roughness Results for Various Anneal Temperatures.

Mat. / Temp.	Pt rms roughness[Å]	Pt ave roughness[Å]	RuO_2 rms roughness[Å]	RuO_2 Ave roughness[Å]
Room	55.6	45.3	70.1	56.7
500℃	22.3	17.5	49.8	39.3
600℃	94.9	77.6	131	105

From the investigations of an oxygen partial pressure effect, we learned that only Ru metal was grown without supplying any O_2 gas. For O_2 partial pressure between 10~40%, we observed a mixed phase of Ru and RuO_2. A pure RuO_2 phase was obtained with O_2 partial pressure of 50%. As-grown films exhibited crystalline feature as shown in Fig. 2. RuO_2 film crystallinity also showed a strong dependance on substrate temperature as was in Pt film. No remarkable crystal structure was observed in the as-grown RuO_2 film. XRD result indicates (101) peak domination at 100℃ and (211) peak for a temperature between 200℃ and 300℃. At the substrate temperature of 400℃, we observed randomized orientation along (100), (101), and (110) planes. Resistivity of Pt and RuO_2 thin film for the various anneal temperatures are given in Fig. 3. As anneal temperature was increased from RT to 700°C, the resistivity of Pt and RuO_2 was decreased from $1x10^{-4}$ to $1x10^{-6}$ Ω-cm. However, almost no change was observed in resistivity for an anneal temperature higher than 600°C. Peeling and pitting phenomenon were observed after 700°C due to TEC difference between Pt and SiO_2. The rms roughness of as-grown and annealed films are shown in Tab. 1. Surface roughness was improved until 500°C annealing temperature, but tend to present increased surface roughness for the temperature higher than 600°C because of the grain growth mechanism.

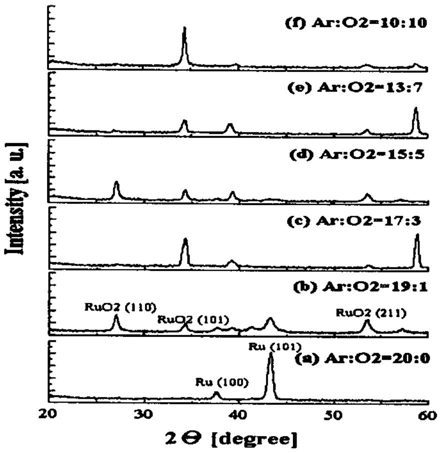

Fig2. XRD diffraction patterns of RuO_2 films for the various O_2 partial pressure.

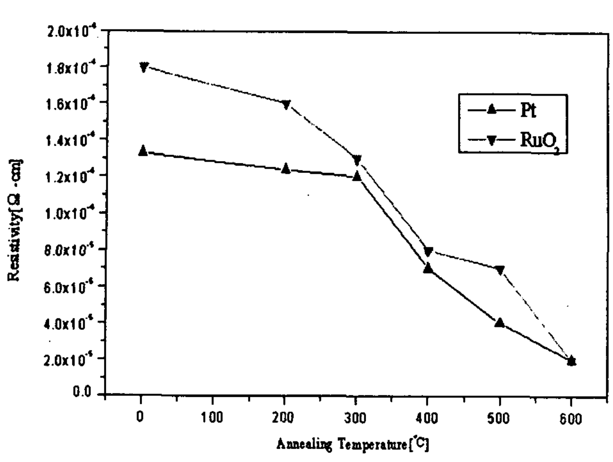

Fig 3. Resistivity of Pt and RuO_2 thin film as a function of post anneal temperature.

4. Conclusions

In this work, we studied the bottom electrodes of ferroelectric thin film using an RF magnetron sputtering technique. The XRD study indicates the substrate temperature at 300°C is recommended for Pt and 200°C for RuO_2 thin film because of the preferred crystal orientation. For O_2 partial pressure between 10~40%, we observed a mixed phase of Ru and RuO_2. A pure RuO_2 phase was obtained with O_2 partial pressure of 50%. This results suggest that we may employ RuO_2/Ru structure as a bottom electrode by simple control of O_2 partial pressure in one step process. The resistivity of Pt and RuO_2 decreased linearly with the increase RTA temperature. The best thin film roughness observed by AFM analysis was 500°C for the post anneal temperature.

Acknowledgement

This work was supported by the academic research fund of Ministry of Education, Republic of Korea, under the contact number of ISRE 97-95 in Seoul National Univ.

Reference

1) Takashi Nakmura, "Preparation of $Pb(Zr,Ti)O_3$ Thin Films on Ir and IrO_2 Electrodes", Jpn. Appl. Phys., Vol. 33, pp. 5297-5210, 1994.
2) Dennis J. Eichorst, et al., "Influence of Processing Conditions on Hillock Formation in Electron-beam Evaporated Platinum/Titanium Films", Integrated Ferroelectrics, Vol. 4. pp. 239-246, 1994.
3) Kazuhide Abe, "PZT Thin Film Preparation on Pt-Ti Electrode by RF Sputtering", Jap. J. Appl. Phys., Vol. 30, No. 9B, pp. 2152-2154, 1993.
4) Hiroshi Majwa, "Preparation and Properties of Ru and RuO_2 Thin Film Electrodes for Ferroelectric Thin Films", Jpn. J. Appl. Phys. Vol. 33, pp. 5223-5226, 1994.
5) Husan N. Al-Shareef, "Bottom Electrodes for Ferroelectric Thin Films", ISIF Proc., p. 181, 1992.