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Bottom electrode optimization for the applications of ferroelectric memory device

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강유전체 기억소자 응용을 위한 하부전극 최적화 연구

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Abstract We have investigated Pt and RuO_2 as a bottom electrode for ferroelectric capacitor applications. The bottom electrodes were prepared by using an RF magnetron sputtering method. Some of the investigated parameters were a substrate temperature, gas flow rate, RF power for the film growth, and post annealing effect. The substrate temperature strongly influenced the surface morphology and resistivity of the bottom electrodes as well as the film crystallographic structure. XRD results on Pt films showed a mixed phase of (111) and (200) peak for the substrate temperature ranged from RT to 200℃, and a preferred (111) orientation for 300℃. From the XRD and AFM results, we recommend the substrate temperature of 300℃ and RF power 80 W for the Pt bottom electrode growth. With the variation of an oxygen partial pressure from 0 to 50 %, we learned that only Ru metal was grown with 0~5 % of O_2 gas, mixed phase of Ru and RuO_2 for O_2 partial pressure between 10~40 %, and a pure RuO_2 phase with O_2 partial pressure of 50 %. This result indicates that a double layer of RuO_2/Ru can be grown in a process with the modulation of gas flow rate. Double layer structure is expected to reduce the fatigue problem while keeping a low electrical resistivity. As post anneal temperature was increased from RT to 700℃, the resistivity of Pt and RuO_2 was decreased linearly. This paper presents the optimized process conditions of the bottom electrodes for memory device applications.

요 약 본 논문은 PZT 박막의 기억소자 응용을 위한 Pt 그리고 RuO_2 박막을 조사하였다. 초고주파 마그네트론 스퍼터링 방법을 이용하여 하부전극을 성장하였으며, 조사된 실험변수는 기판온도, 가스 부분압, RF 전력 그리고 후열처리 등이다. 기판온도는 Pt, RuO_2 박막의 결정구조 뿐만 아니라 표면구조 및 비저항 성분에 크게 영향을 주었다. Pt 박막의 XRD 분석으로 기판온도가 상온에서 200℃까지는 (111) 그리고 (200) 면이 혼재하는 결과를 보였으나 300℃에서는 (111) 면으로 우선 방위 성장 특성을 보였다. XRD와 AFM 해석으로부터 Pt 박막 성장시 기판온도 300℃, RF 전력 80 W가 추천된다. 산소 분압비를 0~50 %까지 가변하여 조사한 결과 산소가 5 % 미만으로 공급되면 Ru 금속이 성장되고, 산소 분압비가 10~40 %까지는 Ru와 RuO_2 상이 공존하였으며 산소 분압비가 50 %에서는 순수한 RuO_2 상만이 검출되었다. 이 결과로부터 RuO_2/Ru 이층 구조의 하부전극 형성이 산소 가스 부분압을 조절하여 한번의 공정으로 성장 가능하며, 이런 구조를 이용하면 금속의 낮은 비저항을 유지하면서도 PZT 박막의 산소 결핍에 의한 기억소자의 피로도 문제를 완화할 것으로 사료된다. 후 열처리 온도를 상온에서부터 700℃까지 증가할 때 Pt와 RuO_2의 비저항 성분은 선형적 감소 추세를 보였다. 본 논문은 강유전체 기억소자 응용을 위한 최적화된 하부전극 제작조건을 제시한다.

1. Introduction

Ferroelectric materials such as PZT, BTO, and BST have been investigated for the development of Gigabit scale dynamic random access memory (DRAM) and nonvolatile memory applications [1-3]. High dielectric constant materials for DRAM devices are required to obtain a proper charge storage in a reduced cell area [4-5]. For the integration of the high permittivity ferroelectric capacitors on Si 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 Si substrates [6-11]. The bottom electrode should not chemically interact with the ferroelectric material nor form a low permittivity compound at the interface in an elevated processing temperature. To meet these requirements, we performed an experimental research work on Pt and RuO_2 as a bottom electrode of thin film capacitors. Various characteristics of thin film Pt and RuO_2 were investigated in terms of a substrate temperature, post anneal temperature, gas flow rate, and RF power. With the examination of Pt and RuO_2 properties, the optimized processing conditions are proposed in this paper.

2. Experimental

Experimental investigations were carried out in the order of sample cleaning, bottom electrode formation, and characterization before and after RTA treatments. Oxidized p-type Si (100) substrates were cleaned in acetone, methanol, and deionized water. A base pressure less than 5×10^{-6} torr was maintained prior to the metal film growth. Platinum thin film was RF sputter deposited using a 2 inch Pt target of 99.999 % purity. The substrate and target were separated by a distance about 6 cm. The Ar gas pressure was kept at about 7 mtorr. Input power was ranged from 40 W to 80 W with substrate temperature variation from RT to 300℃. The RuO_2 thin film was grown by supplying O_2 as a reactive gas source. Ru target with purity of 99.999 % was placed at a distance of 7 cm. The modulation of gas flow rate was carried out to form either RuO_2 or Ru thin film. The substrate temperature was varied from RT to 400℃ for RuO_2 film growth. To find film growth rate we employed an α-step measurement system. Because ferroelectric perovskite structure transformation is occurred at a temperature higher than 500℃, we investigated post anneal temperature effect on bottom electrode using RTA system. Nitrogen gas was introduced at 2.5 lpm during the RTA treatments. An electrical property was investigated by four points probe system (Signatone S-30L). The surface morphological and crystallographic property of the film deposited at different substrate temperatures were characterized by AFM (Mitutoyo Auto-probe CP) and XRD (Mac Science M18XHF-SRA). Figure 1 shows the involved research work procedure of this paper.

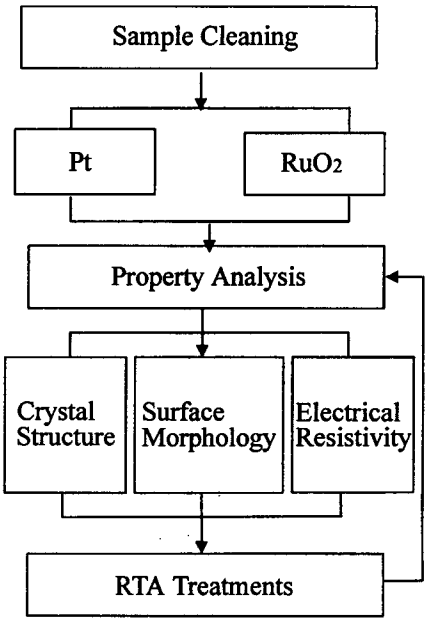

Fig. 1. An employed experimental procedure of the investigation.

3. Results and discussions

Thin film growth rate was investigated in terms of RF power, gas pressure, and substrate temperature as shown in Fig. 2. Deposition rate of Pt thin film showed a linear increase with RF power. The film growth rate increased linearly from 190 Å/min. for an input power of 40 W to 390 Å/min. for 80 W. Whereas, RuO_2 thin film growth rate was decreased as an O_2 partial pressure was changed from 0 % to

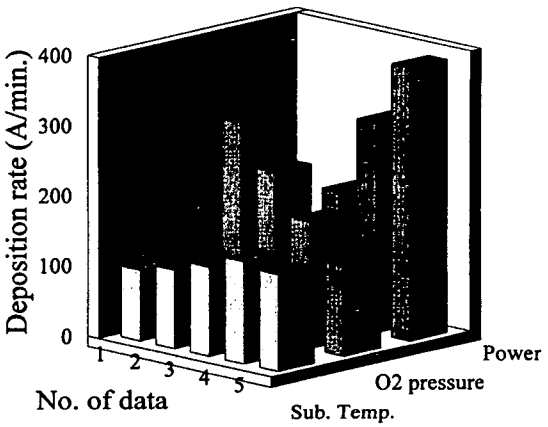

Fig 2. Deposition rate of Pt and RuO_2 thin film as a function of RF power.

50 %. Because the total pressure was fixed to 20 sccm the increased O_2 partial pressure leads to reduced Ar ions, decreased sputtered atoms, consequently low film growth rate. In so far as deposition rate is concerned substrate temperature was the least influencing factor because the temperature changed from RT to 400℃ the rate fluctuated less than 30 Å/min. The deposition rate was increased to a ceratin degree until 300℃ due to the enhanced surface atom mobility. We interpret the reduction of growth rate at the temperature of 400℃ may be contributed by the bouncing back of excess energy atoms at the film surface.

Crystal structure of the thin film was investigated for the various RF power and substrate temperature. Figure 3 shows the XRD results of Pt films as a function of substrate temperature. Over the investigated substrate temperatures, general trend on Pt film structure was (111) preferred orientation. For the temperature less than 100℃ we observed a rather weak (111) and (200) plane. The random orientations at the low temperature are mainly because of the low surface atom mobility. This random structure was transformed to a strongly oriented crystalline structure as the substrate temperature increased higher than 200℃. By the continuation of substrate temperature increase to 300℃, the best XRD result was observed with strong (111) Pt peak intensity. Since (111) peak act as major Pt peak in XRD study, we compared (111) peak intensities for the various substrate temperature and RF power. For the three different RF power there were magnitude variations in XRD (111) peak intensities, however, there were similar trends of substrate temperatures. An additional RF power effect in conjunction with the temperature variations is well illustrated in Fig. 4. A strong RF power influence on Pt film structure was occurred only at the substrate temperature of 200℃. As RF power increased from 40 W to 80 W, the (111) peak intensity changed from 124,000 to 674,000 cps. With the reduced substrate temperature of 200℃ and RF power 80 W, we were able to achieve almost same crystalline structure as in the case of 300℃. To examine the degree of (111) preferential orientation, we calculated XRD peak intensity ratio

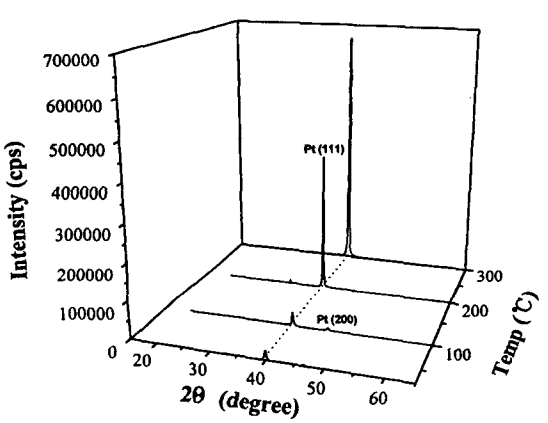

Fig. 3. XRD analysis of Pt film for the various substrate temperatures.

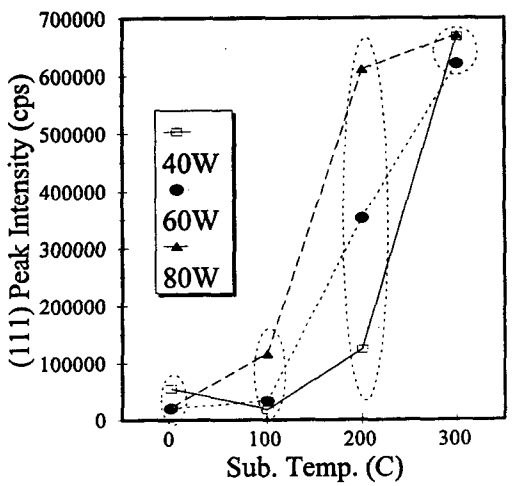

Fig. 4. XRD (111) peak intensity of Pt thin films as a function of substrate temperature and RF input power.

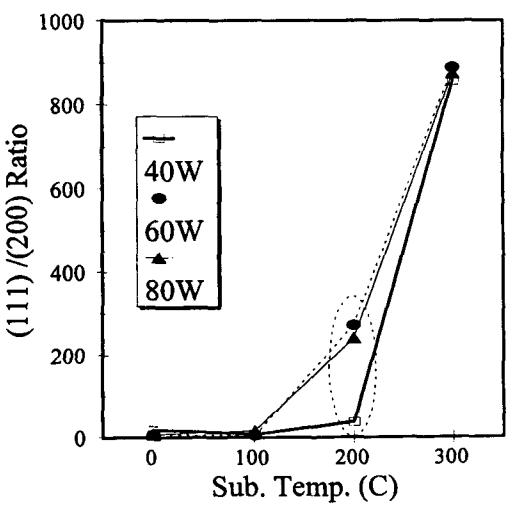

Fig. 5. Intensity ratio of (111)/(200) plane for Pt thin films as a function of substrate temperature and RF input power.

of (111)/(200) as shown in Fig. 5. RF power dependence was very weak for the low and high substrate temperature because the surface energy was either too low or high for a suitable crystalline film growth. At the substrate temperature of 200℃, the (111) preferential crystallinity exhibited a strong dependance on RF input power. As the power increases linearly, so does the (111) preferential orientation which was indicated in (111)/(200) peak intensity ratio. The crystallinity of Pt film was rather strongly influenced by the substrate temperature than RF power.

While Pt film exhibited polycrystal structure at any substrate temperature, RuO_2 film demonstrated no crystalline structure at room temperature. RuO_2 film crystallinity also showed a strong dependance on substrate temperature as was in Pt films. Figure 6 shows the XRD results of RuO_2 films for a growth temperature variation from room temperature to 400℃. For the temperature of 100℃ we observed only (101) RuO_2 peak with 441 cps. The RuO_2 film showed an increased (101) peak intensity to 1040 cps at 200℃. As temperature was increased higher than 200℃, we observed random orientation of RuO_2 film in (110), (101), and (211) plane. At an elevated temperature of 400℃, there were two different phases of a weak Ru (100) and randomized RuO_2 phase. We recommend the substrate temperature of 200℃ for RuO_2 film growth.

From the investigations of an oxygen partial pressure effect at a fixed RF power of 200 W, we learned that only Ru metal was grown with O_2 partial less than 5 %. 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 %. Oxygen partial pressure effect on chemical stoichometry is summarized in Fig. 7. XRD result indicates (101) RuO_2 peak domination at 50 % O_2 partial pressure. For the O_2 partial pressure changed from 10 % to 40 %, we observed randomized orientations of (100), (101), (211) RuO_2, and (100) Ru plane. XRD results indicate that a double layer of RuO_2/Ru can be deposited in situ by the modulation of gas flow rate. This double layer structure may relieve fatigue problems of PZT film while keeping a low electrical resistivity.

We carried out an RTA treatment to examine surface morphology of bottom electrode for the following reasons. The one reason is that a perovskite structure formation is occurred only at an elevated temperature higher than 500℃, therefore, bottom electrode should be subjected to the high temperature in memory device applications. The other one is to see if the Pt and RuO_2 films are stable enough to withstand the high temperature process. Figure 8 shows AFM results on RuO_2 films with and without RTA. Surface roughness was improved after 500℃ anneal treatment. However, an increased surface roughness was observed after the temperature treatment of higher than 600℃. We interpret the degradation of surface roughness is come from the grain growth mechanism. Before and after anneal treatment, AFM study showed a similar trend for the surface roughness of Pt and RuO_2 films. The rms roughness values of as-grown and annealed

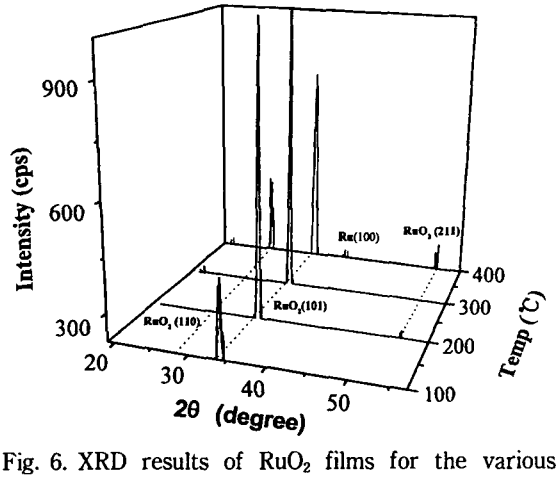

Fig. 6. XRD results of RuO_2 films for the various growth temperatures.

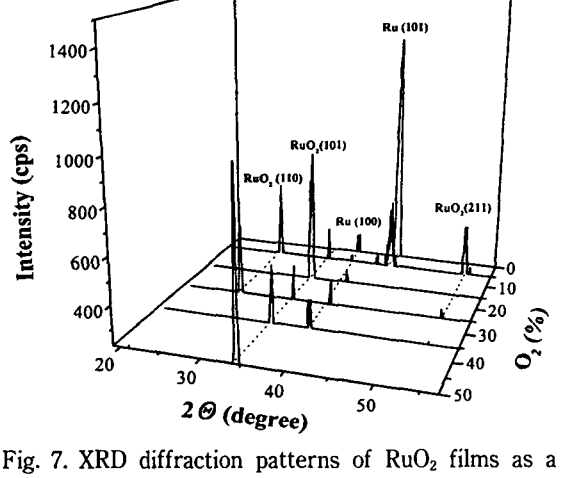

Fig. 7. XRD diffraction patterns of RuO_2 films as a function of O_2 partial pressure.

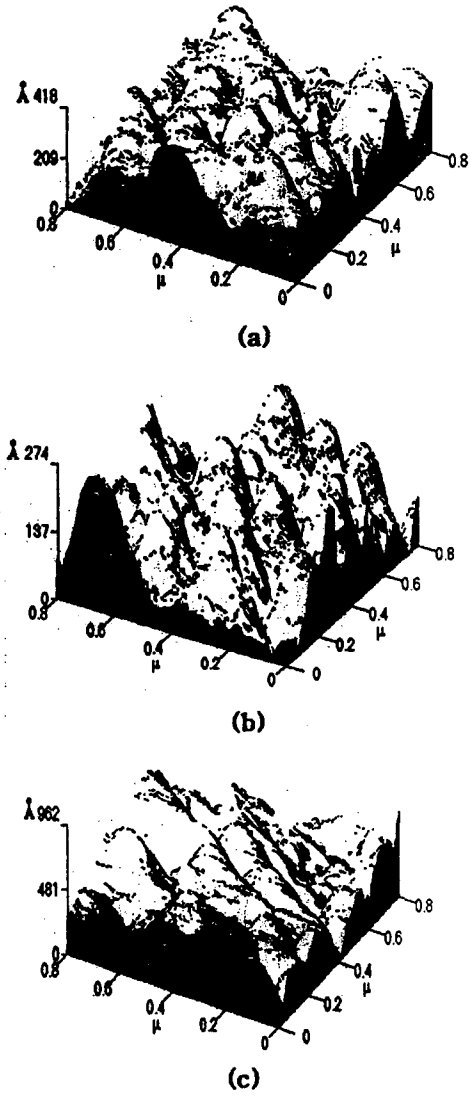

Fig. 8. AFM results on RuO_2 films (a) before, (b) after 500℃, and (c) 600℃ RTA.

films are listed in Table 1. AFM study suggest that a ferroelectric structural transformation has to be carried out at a temperature less than 600℃ for Pt and RuO_2 electrode.

Electrical resistivity of Pt and RuO_2 thin film for the various anneal temperatures is illustrated in Fig. 9. As anneal temperature was increased from RT to 700℃, the resistivity of Pt and RuO_2 was decreased from 1×10^{-4} to 1×10^{-6} Σ-cm. Because of high temperature stability of Pt, almost no change was monitored in resistivity for the anneal temperature less than 300℃. However, RuO_2 exhibited a linear decrease with an increase of anneal temperature. XRD study indicates a structural modification of RuO_2 film at a temperature higher than 400℃. The cause of reduced resistivity of RuO_2 films at the low temperature is considered as an evolution of oxygen out of RuO_2 films leaving behind Ru metallic phase. Peeling and pitting phenomenon were observed after 700℃ due to TEC difference between Pt and SiO_2. AFM and resistivity examinations suggest post anneal temperature should be maintained less than 600℃.

Table 1
AFM roughness results of Pt and RuO_2 thin films

Mat. / Temp.	Pt		RuO_2	
	rms roughness [Å]	avg roughness [Å]	rms roughness [Å]	avg 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	131.0	105.0

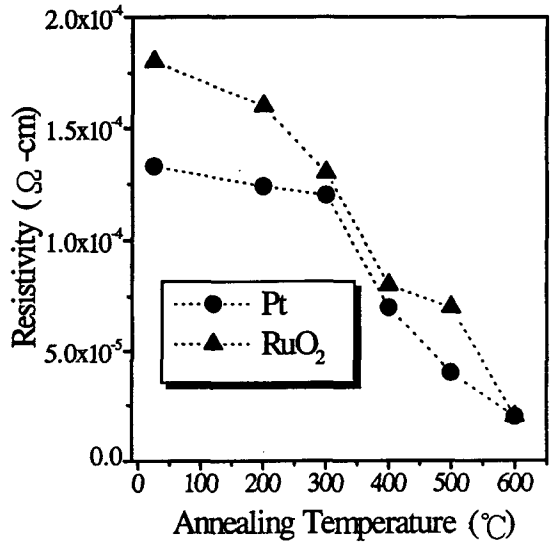

Fig 9. Resistivity versus anneal temperature for Pt and RuO_2 films.

4. Conclusions

In this work, we studied the bottom electrodes of ferroelectric capacitors using an RF magnetron sputtering system. Pt and RuO_2 film growth rate was showed a linear increase with RF power and decrease with O_2 partial pressure. From the structural investigations the substrate temperatures

of 300℃ for Pt and of 200℃ for RuO_2 bottom electrode are recommended 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 can fabricate RuO_2/Ru double layer structure as a bottom electrode by simple variation of O_2 partial pressure in one step process. The resistivity of Pt and RuO_2 decreased linearly with the increased RTA temperature between 300 and 600℃ and saturated higher than 600℃. The best thin film roughness before and after RTA was achieved after 500℃ RTA treatment. This result suggest that our future research work should be directed to achieve ferroelectric film at the processing temperature of 500℃.

Acknowledgments

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