Investigation of the surface modification for Ru and RuOx films using a post-treatment method for high-dielectric applications

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The effect of post-treatment on the surface modification for Ru and RuOx films was investigated. The surface morphology of Ru film oxidized by N2O plasma was observed to be much smoother than that by rapid thermal oxidation. In particular, the leakage current property of the Ru film oxidized by N2O plasma was significantly improved due to suppression of heterogeneous grain growth and the Ru–O bonds formed. After post-treatment, otherwise, oxygen is fully diffused through the RuOx layer, producing a porous amorphous microstructure. In addition, the barrier properties for the Ru/TiN/poly-Si/Si contact system are better than that for the RuOx/TiN/poly-Si/Si contact system. Therefore, N2O plasma oxidation can be suggested as a post-treatment method and the Ru film can be proposed as a bottom electrode to improve the electrical properties of dielectric film at the dielectric film/Ru bottom electrode interface.

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1. Introduction

SiO2/Si3N4 films [1] have been used as dielectric layers in dynamic random access memory (DRAM) capacitor structures. The charge-storage capacity required for device operation has been satisfied by thinning the dielectric layer and adopting a three-dimensional structure instead of a simple planar geometry. When the SiO2/Si3N4 dielectric film is used in the capacitor for ultra large-scale integration and beyond, the dielectric film should be thinned to its physical limits where further thinning results in large direct tunneling currents. For 256-Mbit generation and beyond, the SiO2/Si3N4 layer cannot be used as a dielectric material because the required capacitance per cell area cannot be obtained by thinning and increasing the cell area. To overcome these problems and increase device integrity, high dielectric constant oxide with perovskite structure, barium strontium titanate (BST) (Ba1–xSrxTiO3) [2] is introduced to memory devices. Although they have much merit, with a high dielectric constant and good para(ferro)electric properties, their applications on real devices still cause serious problems due to the high-temperature, oxidizing ambient processes required.

Ruthenium (Ru) [3] and ruthenium dioxide (RuO2) [4] have been proposed as bottom electrode materials for the high-density capacitors because they show high electrical conductivity, and ease of dry etching. Under deposition and thermal-treatment processes of the dielectric films, however, oxygen in dielectric films can react with bottom electrodes and form an interfacial layer between the dielectric films and the bottom electrodes. This is supported by the results reported by others that the second phase is formed at the dielectric/Ru electrode interface during the deposition of BST [3, 5, 6, 8]. In the case of the Ru bottom electrode, where either annealing or deposition is performed in oxygen ambient, in particular, its surface morphology is observed to be much rougher [6–8]. These should cause a degradation of capacitor performance. Based on the above consideration, it is believed that the suppression of the interfacial layer as well as improvement of interfacial morphology at the dielectric/bottom electrode interface is expected to enhance the electrical properties of high-dielectric films.

In this study, we concentrated on the surface modification of each Ru and RuOx film using rapid thermal annealing in an oxygen ambient (RTO) and N2O plasma oxidation to overcome the interface-related problems between the dielectric films and the bottom
electrode. Such a post-treatment method is introduced to form binding between oxygen and the Ru. The oxidation kinetics is strikingly different with each post-treatment method because there is a difference of chemical activity for reaction between neutral atoms or molecules in RTO and negative oxygen ions in the N₂O plasma oxidation. The Ru–O chemical bonds formed after post-treatment would decrease the chemical affinity for oxygen in the dielectric films during deposition or post-annealing processes, followed by a decrease of the driving force for chemical reaction between the dielectric film and the Ru–O bonds formed. In particular, it is expected to result in some difference in the surface morphology due to the different chemical potential for oxidation species. To find an appropriate bottom electrode and post-treatment method for an improvement of the electrical properties, in this work, we investigated various properties for the Ru and RuOₓ films, respectively, and compared them as a function of the post-treatment (RTO and N₂O plasma) at 400 °C for 1 and 3 min.

2. Experiment

An 8-inch Si wafer was used as a substrate in this work. After cleaning the substrate by removing the native oxide on the Si surface, a SiO₂ layer was grown by thermal oxidation, followed by a Ta₂O₅ film, as an adhesion layer, by metal organic chemical vapor deposition (MOCVD). Ru or RuOₓ films were deposited on the Ta₂O₅/SiO₂/Si substrates in a direct-current (d.c.) sputtering system with a 7-inch Ru target in a mixture of Ar and O₂. RuO₂ films were deposited in a mixture of Ar with 47% O₂. The base pressure in the sputtering chamber was less than 5.3 × 10⁻⁵ Pa and the total working pressure during sputtering was 0.4 Pa. Based on the preliminary experiments, such as deposition rate, resistivity, crystallinity, stress, and adhesion, the substrate temperature and d.c. sputtering power during both the Ru and RuOₓ deposition were determined to be 200 °C and 250 W, respectively. To investigate the depth of oxygen diffusion, the thickness of both the Ru and RuOₓ film was fixed at 100 nm. After deposition of both the Ru and RuOₓ layers, samples were annealed in oxygen atoms or a molecules and oxygen ions ambient for 1 min and 3 min at 400 °C using RTO and N₂O plasma, respectively.

To investigate the effect of post-treatment on the leakage current properties, 30-nm thick BST films were deposited by MOCVD using Ba(thd)₂–pmdt(Ba(2,2,6,6–tetramethylheptane–3,5–dionate)₂–1,1,4,7,7–pentamethylidithielenetriamine), Sr(thd)₂–pmdt (Sr(2,2,6,6–tetramethylheptane–3,5–dionate)₂–1,1,4,7,7–pentamethylidithielenetriamine) and Ti(O-i–Pr)₂(thd)₂ (Ti(iso–propoxido)(2,2,6,6–tetramethylheptane–3,5–dionate)₂) metal sources at a substrate temperature of 400 °C and the total working pressure during deposition was 2.7 × 10⁻² Pa. Argon gas was used as a carrier to deliver the evaporated source to the process chamber and O₂/N₂O gas was employed as an oxidant gas. The flow rate of Ar gas was 400 sccm and that of O₂/N₂O gas was 100/100 sccm. After deposition of BST film, two-step annealing was carried out using rapid thermal annealing in a nitrogen ambient (RTN, 700 °C for 3 min) for its crystallization and then in an oxidizing ambient (RTO, 420 °C for 5 min) for supplying oxygen into the BST film. To compare the electrical properties of BST dielectric film, the Ru films were prepared with and without post-treatment. To investigate the leakage current for the Pt(100 nm)/BST(30 nm)/Ru(100 nm)/TaOₓ/SiO₂/Si structure, current–voltage (I–V) measurements were carried out between the Pt and Ru film. One probe that is varied from −3 V to +3 V is contacted to Pt and another one, which is the ground state, is probed to the Ru film. In this work, all I–V curves were obtained from 100 × 100 μm in contact size.

Thickness and surface morphology of the deposited films were examined by scanning electron microscopy (SEM). Auger electron microscopy (AES, 10 keV, 1 nA) was used for depth profiling of the layer structures. The X-ray diffraction (XRD) was performed using CuKα radiation with glancing angle incidence (incident X-ray angle, θ = 5°) in order to identify phases. Transmission electron microscopy (TEM) was used for the microstructural analysis of the deposited films. The binding state of the annealed samples was investigated by X-ray photoelectron microscopy (XPS, 3 keV, 1 μA). The sheet resistance of the films was measured by a 4-point probe method.

3. Results and discussion

Fig. 1 shows the variation of the sheet resistance for both the Ru/Ta₂O₅/SiO₂/Si and RuOₓ/Ta₂O₅/SiO₂/Si layer structures depending on the post-treatment method and time at 400 °C. Here, the thickness of both the Ru and RuOₓ layers was 100 nm. For both layer structures, the sheet resistance is decreased gradually with increasing annealing time compared to that in the as-deposited state.

![Figure 1](image-url)  
**Figure 1** Variation of sheet resistance for both Ru/Ta₂O₅/SiO₂/Si and RuOₓ/Ta₂O₅/SiO₂/Si systems with different post-treatment methods and times.