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Chemical Vapor Deposition of Ru and Its Application in (Ba, Sr)TiO3 Capacitors for Future DRAM

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1. Introduction

Ru is one of the most promising materials for electrodes of (Ba, Sr)TiO_3 (BST) capacitors used in dynamic random access memories (DRAMs)[1]. In giga-bit DRAMs, 3-dimensional capacitors will be necessary even if we will use BST as capacitor dielectrics[2]. Therefore, chemical vapor deposition (CVD) is considered to be essential as film preparation method for both Ru electrodes and BST dielectrics. Although numerous papers have been reported for CVD of BST, there is few reports for CVD of Ru aiming at DRAM application.

In this paper, we successfully fabricated Ru thin films with low resistivity and excellent step coverage and applied them to the electrodes for BST capacitors.

2. Experimental

Ru films were deposited using cold wall type CVD chamber. Bis-(cyclopentadienyl)ruthenium ($Ru(C_5H_5)_2$: $Ru(Cp)_2$) heated at 130℃ was used as a source material and carried by Ar. O_2 was added to decompose $Ru(Cp)_2$ gas. The flow rate ratio of Ar/O_2 was 2. The chamber pressure was 0.2 Torr and the substrate temperature varied from 230 to 315℃. Thermal treatment at 650℃ in Ar for 1min (RTA) was carried out after Ru film deposition. Film thickness and step coverage were characterized by scanning electron microscope (SEM). Crystalline structure was analyzed using X-ray diffraction (XRD). Resistivity was measured in terms of 4-probes method.

To fabricate capacitors, 60-nm-thick BST film was deposited by CVD on RTA treated Ru film prepared by CVD. The deposition conditions of BST-CVD were described in Ref. [3]. To crystallize BST film, RTA at 650℃ in Ar for 1 min was performed after BST deposition.

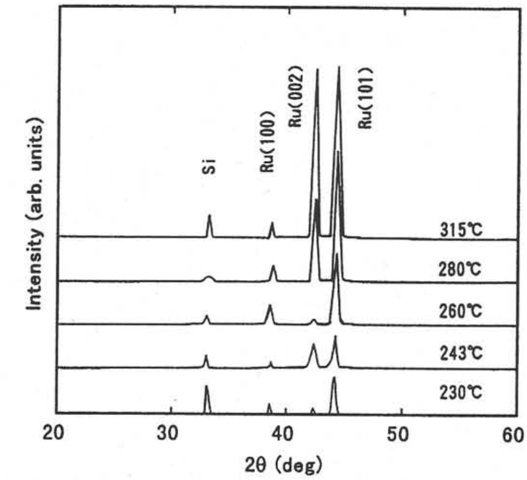

Fig. 1 X-ray diffraction spectra of 100-nm-thick Ru films.

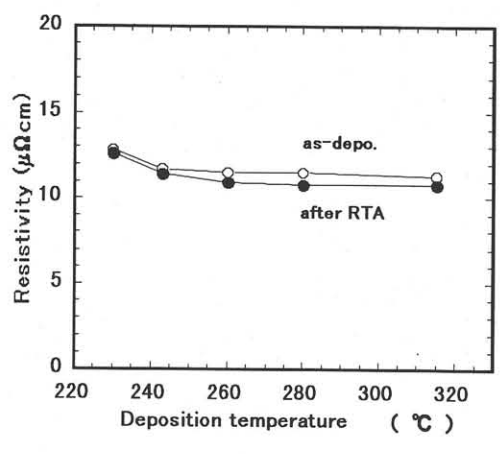

Fig. 2 Resistivity of Ru films before and after RTA at 650℃ in Ar for 1 min.

3. Results and Discussion

Figure 1 shows XRD spectra of 100-nm-thick Ru film deposited on SiO_2 film as a function of deposition temperature. In spite of using O_2 during deposition, no RuO_2 peaks were observed. Intensities of diffraction peaks attributed to Ru increased as the rise of deposition temperature. From these spectra, it is clear that CVD-Ru film has random orientation.

Resistivity of Ru films before and after RTA at 650℃ in Ar for 1 min is shown in Fig. 2. Resistivity increased with the lowering of deposition temperature. The increase of resistivity is due to increase of residual impurities such as carbon and hydrogen and decrease of grain size. After RTA, resistivity slightly decreased. This is because decrease of impurities and grain growth of Ru. These films showed low resistivity of about 12 $\mu\Omega$ cm. From the results of XRD and resistivity, it is considered that the grain size of Ru deposited at high temperatuer is larger than that of Ru deposited at low temperature.

Figure 3 shows Arrhenius plots of the growth rate of Ru film. The deposition was controlled by the surface reaction kinetics as the rate limiting step with activation energy of 2.48 eV below 250℃ and by the mass transport process above 250℃. To obtain good step coverage, Ru film is desired to be controlled by the surface reaction kinetics.

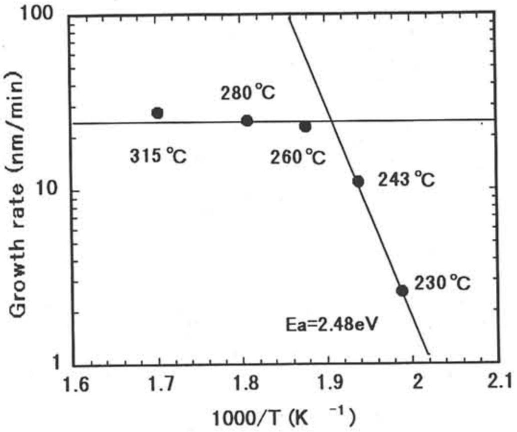

Fig. 3 Arrhenius plots of the growth rate of Ru film.

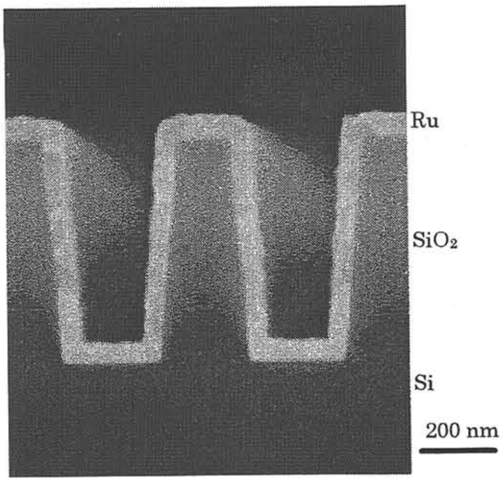

Fig. 4 Cross-sectional SEM image of Ru film deposited at 230℃.

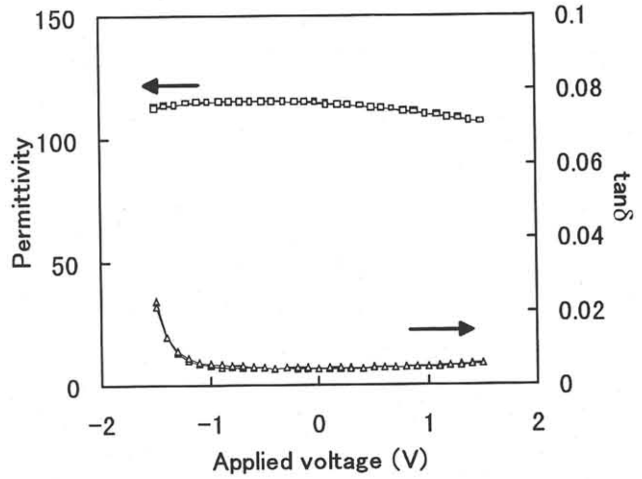

Fig. 5 Permittivity and dielectric loss of the BST capacitor with CVD-Ru bottom electrode.

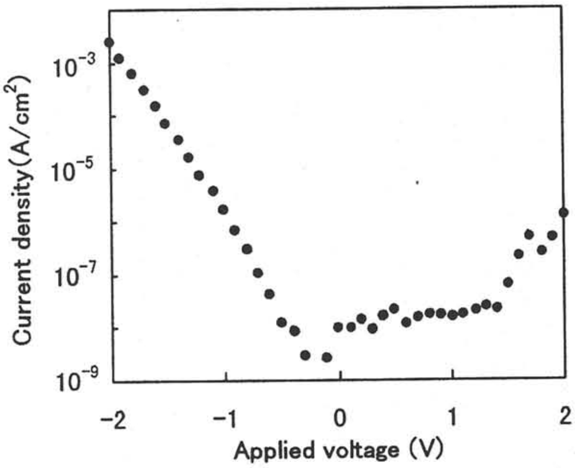

Fig. 6 Leakage current characteristics of the BST capacitor with CVD-Ru bottom electrode.

In order to evaluate the step coverage, Ru film was deposited at 230℃ on the patterned substrate with aspect ratio of 1.8. Cross-sectional SEM image is shown in Fig. 4. Since Ru deposition is performed at the low temperature below 250℃, excellent step coverage is obtained.

The electrical properties of $Ba_{0.25}Sr_{0.75}TiO_3$ capacitor with CVD-Ru bottom electrode and sputtered Ru top electrode were measured. Permittivity and dielectric loss by capacitance-voltage measurement are shown in Fig. 5. Maximum relative dielectric constant of 120 and low dielectric loss were obtained. Figure 6 shows leakage current characteristics. The leakage current of plate (+) which was equivalent to the injection of electrons from CVD-Ru bottom electrode into BST film was sufficiently suppressed. The larger leakage current of plate (-) than plate (+) is considered to be due to the sputtering damage during the top electrode formation.

4. Conclusion

We studied on CVD of Ru as electrodes of BST capacitors used in DRAMs. We successfully fabricated Ru thin films with low resistivity and excellent step coverage by low temperature CVD using $Ru(Cp)_2$ and O_2. The BST capacitor using the Ru electrode prepared by CVD showed good electrical characteristics.

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