Improved Oxygen Diffusion Barrier Properties of Ruthenium-Titanium Nitride Thin Films Prepared by Plasma-Enhanced Atomic Layer Deposition

Seong-Jun Jeong¹, Doo-In Kim², Sang Ouk Kim¹, Tae Hee Han¹, Jung-Dae Kwon³, Jin-Seong Park⁴, and Se-Hun Kwon².*

¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
²National Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 609-735, Korea
³Center for Convergence Materials and Technology, Korea Institute of Materials Science, Changwon 641-010, Korea
⁴Department of Materials Science and Engineering, Dankook University, Cheonan 330-714, Korea

Ru–TiN thin films were prepared from bis(ethylcyclopentadienyl)ruthenium and tetrakis(dimethylamino)titanium using plasma-enhanced atomic layer deposition (PEALD). The Ru and TiN were deposited sequentially to intermix TiN with Ru. The composition of Ru–TiN films was controlled precisely by changing the number of deposition cycles allocated to Ru, while fixing the number of deposition cycles allocated to TiN. Although both Ru and TiN thin films have a polycrystalline structure, the microstructure of the Ru–TiN films changed from a TiN-like polycrystalline structure to a nanocrystalline on increasing the Ru intermixing ratio. Moreover, the electrical resistivity of the Ru₀.⁶⁷–TiN₀.₃₃ thin films is sufficiently low at 190 μΩ·cm and was maintained even after O₂ annealing at 750 °C. Therefore, Ru–TiN thin films can be utilized as an oxygen diffusion barrier material for future dynamic (DRAM) and ferroelectric (FeRAM) random access memory capacitors.

Keywords: Plasma-Enhanced Atomic Layer Deposition, Oxygen Diffusion Barrier, Ruthenium-Titanium Nitride, FRAM, DRAM.

1. INTRODUCTION

Dynamic random access memory (DRAM) and ferroelectric random access memory (FeRAM) are the most common types of random access memory (RAM) used to store data in volatile or nonvolatile capacitors within integrated circuits. These RAMs have been highly integrated to achieve electrical properties that include sufficient capacitance and a low leakage current per cell.¹ However, the high integration causes critical issues in terms of the diffusion barrier, dielectric or ferroelectric properties, and the bottom electrode.²–⁴

The oxidation of bottom electrodes is a serious problem for future DRAM and FeRAM because of the deposition of high-permittivity materials at temperatures above 500 °C in an oxygen atmosphere or post-annealing at above 650 °C to improve the chemical and electrical properties.¹,⁵ In order to settle this issue, oxygen diffusion barriers have been proposed in various studies. However, a superior oxygen diffusion barrier is still required due to the high reactivity and fast diffusivity of oxygen at high temperatures. Furthermore, as the aspect ratio of capacitor structures increases with high integration, the three-dimensional conformality of the oxygen diffusion barrier has become important.⁶ Recently, ruthenium (Ru) and ruthenium dioxide (RuO₂) have received attention as oxygen diffusion barrier materials because they can prevent oxygen diffusion during the fabrication and annealing of dielectrics.⁷ However, the results are not always satisfactory because these substances have a columnar grain structure, and such grain boundaries provide a fast diffusion path for oxygen.

Here, we investigate Ru–TiN thin films prepared using a plasma-enhanced atomic layer deposition (PEALD) method to prevent oxygen diffusion in future DRAM and FRAM capacitors. In addition, the relationship between film microstructure and oxygen diffusion barrier properties of the films is investigated systemically.
2. EXPERIMENTAL DETAILS

2.1. Materials

Ru–TiN films were deposited on 100-nm-thick thermally grown SiO2 film formed on Si substrates using PEALD at 200 °C and 3 Torr. The respective Ti and Ru precursors were tetrakis(dimethylamino)titanium [TDMAT] and bis(ethylcyclopentadieny) ruthenium [Ru(EtCp)2]. The TDMAT and Ru(EtCp)2 were contained in bubblers and heated at 40 and 80 °C, respectively. At these temperatures, the respective vapor pressures of TDMAT and Ru(EtCp)2 are 0.309 and 0.178 Torr.

2.2. Design of the Supercycle for Ru–TiN Films

Ru–TiN films were deposited by repeating a supercycle that consisted of separate groups of subcycles dedicated for Ru and TiN, respectively. Each subcycle consisted of several unit cycles, and four consecutive pulses were supplied in a unit cycle. The unit cycle for TiN consisted of a TDMAT vapor pulse with Ar carrier gas (50 sccm), a purge pulse with Ar (50 sccm), a pulse for an exposure to N2 gas (100 sccm), and an Ar (50 sccm) purge pulse. The unit cycle for Ru consisted of a Ru(EtCp)2 vapor pulse with Ar carrier gas (75 sccm), a purge pulse with Ar (50 sccm), a pulse for an exposure to a mixed gas plasma with N2 (100 sccm) and H2 (100 sccm), and an Ar (50 sccm) purge pulse. Ar gas (100 sccm) was supplied to the reactor continuously during deposition. Radio frequency (rf) plasma was used at a fixed electrical power of 100 W. The intermixing ratios of Ru in the deposited films were controlled by changing the number of unit cycles in one Ru subcycle. The number of unit cycles allocated to the TiN subcycle was fixed at one.

2.3. Characterizations

Film thickness was investigated using field emission scanning electron microscopy (FESEM) and film composition was analyzed using 9.0 MeV He2+ Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES). The microstructures of the films were detected with X-ray diffractometry (XRD) using Cu Kα radiation at 1.5405 Å and high-resolution transmission electron microscopy (HRTEM). To evaluate the electrical characteristics, the sheet resistance of the films was measured using the four-point probe test. The oxygen barrier properties of Ru–TiN films were compared with that of TiN and Ru films. The specimens were treated with a rapid thermal annealing (RTA) system at temperatures of 500–800 °C for 30 min in ambient O2. During the RTA process, the O2 flow rate was maintained at 300 sccm and the total pressure was maintained at 3 Torr. The performance as an oxygen diffusion barrier was evaluated by comparing the variation in the sheet resistance and the formation of RuO2 or TiO2 phases before and after the RTA process.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the change in thickness of a TiN film grown on Ru and a Ru film deposited on TiN substrate as a function of the number of deposition cycles. As can be seen, the deposition rate of PEALD–TiN is about 0.169 nm/cycle when the TDMAT pulse time exceeds 4 s, and that of PEALD–Ru is 0.039 nm/cycle at a Ru(EtCp)2 pulse time of 7 s. The resistivities of these films were 970 and 13 μΩ·cm, respectively. Figure 1(b) shows the dependence of the thickness/cycle (nm/cycle) on the intermixing ratio of supercycles consisting of Ru and TiN unit cycles.
The deposition rate of the Ru–TiN thin film increased with the number of Ru sequences. In addition, the atomic ratio of the Ru–TiN films depended on the number of Ru unit cycles, as also indicated in Figure 1(b). The resulting electrical resistivity of the Ru0.67(TiN)0.33 thin films was sufficiently low as 190 μΩ cm. In Figure 1(b), however, the deposition rate of the Ru–TiN film was lower than the simple calculated sum of \([\text{deposition rate of TiN}] + N \times [\text{deposition rate of Ru}]\). As shown in the inset of Figure 1(a), less Ru(EtCp)2 chemisorbed on the TiN surface than on the homogeneous Ru surface.8

The crystallinity of the prepared films was investigated using cross-sectional micrographs and selected area diffraction patterns. As shown in Figure 2, the PEALD–Ru and PEALD–TiN thin films grow as columnar structures, whereas the immediate suppression of the columnar growth was apparent for Ru–TiN films. Figure 3 shows the selected area diffraction patterns of films with various compositions, including TiN, Ru0.13(TiN)0.87, Ru0.40(TiN)0.60, and Ru0.67(TiN)0.33. The microstructure of the TiN film is polycrystalline, as shown in Figure 3(a). However, the microstructure of the Ru–TiN films becomes nanocrystalline, consisting of TiN nanocrystals embedded in amorphous Ru-rich phase matrix, with an increasing Ru intermixing ratio up to 0.67. This suggests that crystallization between Ru grains and TiN grains is interrupted by intermixing with Ru and TiN, and the microstructure of Ru–TiN thin films has a nanocrystalline structure above 500 °C. The deposition rate of the Ru–TiN thin film increased with the number of Ru sequences. In addition, the atomic ratio of the Ru–TiN films depended on the number of Ru unit cycles, as also indicated in Figure 1(b). The resulting electrical resistivity of the Ru0.67(TiN)0.33 thin films was sufficiently low as 190 μΩ cm. In Figure 1(b), however, the deposition rate of the Ru–TiN film was lower than the simple calculated sum of \([\text{deposition rate of TiN}] + N \times [\text{deposition rate of Ru}]\). As shown in the inset of Figure 1(a), less Ru(EtCp)2 chemisorbed on the TiN surface than on the homogeneous Ru surface.8

The crystallinity of the prepared films was investigated using cross-sectional micrographs and selected area diffraction patterns. As shown in Figure 2, the PEALD–Ru and PEALD–TiN thin films grow as columnar structures, whereas the immediate suppression of the columnar growth was apparent for Ru–TiN films. Figure 3 shows the selected area diffraction patterns of films with various compositions, including TiN, Ru0.13(TiN)0.87, Ru0.40(TiN)0.60, and Ru0.67(TiN)0.33. The microstructure of the TiN film is polycrystalline, as shown in Figure 3(a). However, the microstructure of the Ru–TiN films becomes nanocrystalline, consisting of TiN nanocrystals embedded in amorphous Ru-rich phase matrix, with an increasing Ru intermixing ratio up to 0.67. This suggests that crystallization between Ru grains and TiN grains is interrupted by intermixing with Ru and TiN, and the microstructure of Ru–TiN thin films has a nanocrystalline structure above 500 °C.

![Fig. 2. Cross-section view HRTEM images of (a) PEALD–Ru film on SiO2; (b) PEALD–TiN film on SiO2; and (c) PEALD–Ru0.67(TiN)0.33 film on SiO2.](image)

![Fig. 3. Selected area diffraction patterns of (a) PEALD–TiN film; (b) Ru0.13(TiN)0.87 film; (c) Ru0.40(TiN)0.60 film; and (d) Ru0.67(TiN)0.33 film.](image)

![Fig. 4. SEM micrographs of PEALD–Ru0.67(TiN)0.33 film on a trench structure formed in ALD-HfO2 with an opening width of 146 nm and a depth of 1480 nm.](image)

![Fig. 5. (a) Sheet resistance variation of PEALD–TiN, PEALD–Ru, and PEALD–Ru0.67(TiN)0.33 films (with various compositions) after O2 annealing for 30 min, and (b) 2θ XRD patterns of the PEALD–Ru0.67(TiN)0.33 film at a temperature range of 500–800 °C.](image)
a Ru intermixing ratio of 0.67. The step coverage (ratio of thickness between the top and bottom corners) of the Ru$_{0.67}$–TiN$_{0.33}$ film on a trench structure with an opening width of 146 nm and a depth of 1480 nm (i.e., an aspect ratio of about 10.2:1) was confirmed to be 99%, as shown in Figure 4.

The variation of the sheet resistance of PEALD–TiN, PEALD–Ru, and PEALD–Ru$_x$–(TiN)$_{1-x}$ films (with various compositions) after O$_2$ annealing for 30 min was measured to investigate the properties of the oxygen diffusion barrier. The annealing temperature was varied from 500 to 800 °C. As shown in Figure 4(a), the sheet resistances of the TiN and Ru films increased abruptly after annealing at 550 and 600 °C, respectively. By contrast, the abrupt increase in the sheet resistance was not observed for Ru$_x$–(TiN)$_{1-x}$ films ($x > 0.40$) even at 700 °C. To confirm the reason for the increase in the sheet resistance of the Ru–TiN film over 750 °C, the XRD pattern of the Ru$_{0.67}$–TiN$_{0.33}$ film was investigated. In Figure 4(b), the peaks generated from RuO$_2$ begin to appear at 2θ = 27.9° and 34.9° after heating to 700 °C. The formation of the RuO$_2$ phase causes the sheet resistance of the Ru–TiN film to increase due to the higher resistivity of RuO$_2$. However, the amount of RuO$_2$ seems to be relatively small to affect the resistivity of Ru–TiN films when annealed at 750 °C, and it did not appear in Figure 4(a).

4. CONCLUSIONS

Ru–TiN thin films deposited sequentially by intermixing TiN with Ru were prepared successfully by PEALD at 200 °C and 3 Torr with sufficient step coverage. The microstructure of the Ru–TiN films changed to a nanocrystalline structure on increasing the Ru intermixing ratio, and both the Ru and TiN thin films had polycrystalline structures. The Ru–TiN barrier prevented oxygen diffusion more effectively than did either PEALD–TiN or PEALD–Ru because the nanocrystalline structure of the Ru–TiN thin films prevented oxygen diffusion through grain boundaries. Moreover, the electrical resistivity of the Ru–TiN thin films was sufficiently low, at 190 μΩ·cm, and it did not change very much even after O$_2$ annealing at 750 °C. Therefore, Ru–TiN thin film is a very promising material for achieving a superior oxygen diffusion barrier in future DRAM and FRAM capacitors.

Acknowledgment: This research was supported by National Core Research Center program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2010-0001-226) and by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References and Notes