UV-O₃ treatment effects on structural changes of low-k thin films

Jaeyeong Heo, Dail Eom, Hyeong Joon Kim*

School of Materials Science and Engineering, Seoul National University
San #56-1, Sillim-9 dong, Gwanak-gu, Seoul, 151-744, Korea

Abstract

The UV-O₃ treatment effects on the structural properties of low-k films as a function of the treatment time were investigated in this study. The thickness of the samples proportionally decreased with the surface treatment time due to highly reactive ozone and the process gradually modified surface layer more SiO₂-like. Excessive treatment of longer than 60 s adversely affected the low-k film, increasing the dielectric constant of underlying low-k film. After the UV-O₃ treatment for the optimized treatment time of 60 s, the poor nucleation problem of Ru deposition was solved and fully-covered Ru film on low-k film was obtained.

Keywords: low-k; UV-O₃; surface modification; Ru; diffusion barrier

1. Introduction

As microelectronic circuits become increasingly smaller, the connections between the transistors come to have a greater influence on the circuit performance than the devices themselves [1]. The interconnect performance is determined by the product of R, the resistance of the metal lines, and C, the capacitance of the intermetal dielectric. The capacitance can be reduced by replacing the SiO₂ insulator (k=4.2) with a low dielectric constant material, otherwise known as a low-k material. The introduction of porosity is one of the methods of obtaining a low dielectric constant. Similarly, due to its low resistivity, copper (Cu) has replaced aluminum in order to reduce the resistance. Copper interconnects require a barrier layer to prevent the diffusion of Cu into the adjacent dielectric, and physical vapor deposition (PVD) is most widely used for this purpose. However, at the 45nm node or below, the step coverage provided by the PVD technique will be too poor to extend to the next generation and the effective resistivity of the line will also increase. Atomic layer deposition (ALD), on the other hand, has the capability of producing ultra-thin conformal films in the sub-nm range and, thus, could be a potential candidate [2,3].
Regardless of the choice of low-\textit{k} dielectric and barrier metal, one major obstacle to the adoption of the ALD process is the penetration of the precursor materials into the porous low-\textit{k} dielectrics, which may affect the dielectric stability and eventually the circuit performance [4]. Accordingly, various surface modification methods have been proposed and extensively investigated. Among the modification methods, UV-O3 treatment has been reported to effectively seal the surface without any adverse modification of the underlying low-\textit{k} film [5,6]. In this paper, we studied the changes in the structural and electrical properties of low-\textit{k} films with the UV-O3 treatment time and verified the surface modification effect by depositing Ru thin film, a candidate metal barrier, using ALD process.

2. Experimental details

Low-\textit{k} a-SiOC:H thin films were deposited by a PECVD method using bis-trimethylsilyl methane (BTMSM, H$_3$C$_3$Si-CH$_2$Si-C$_3$H$_9$) as the precursor [7]. The deposition was performed at 25 °C and was followed by annealing in N$_2$ ambient at 450 °C for 30 min. The thickness of the annealed sample was about 200 nm. UV-O$_3$ treatment was performed in a homemade ALD chamber equipped with a commercially available low-pressure mercury UV lamp at room temperature. Schematic diagram of UV-O$_3$ treatment chamber is described elsewhere [8]. Various treatment times were used, viz. 30, 60, 300, 600, and 1200 s. Ru films were deposited in a shower-head type ALD chamber. The process conditions are described elsewhere in detail [9].

The structure of the films was analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), water contact angle, and scanning electron microscopy (SEM). The electrical properties were measured after the fabrication of the MIS (Al/low-\textit{k}/Si) capacitor.

3. Results and discussion

Figure 1 shows the XRR spectra of 50 nm thick as-deposited and UV-O$_3$ treated low-\textit{k} films. The thickness of the UV-O$_3$ treated samples for for 20 min decreased by 5%, which confirmed by the increase in the distance between the adjacent interference maxima. As the treatment time increases, it appears that surface layer is etched-out due to highly oxidative and reactive nature of ozone. The film density also can be calculated with the critical angle. The simulated density of the as-deposited film was 1.32. After the surface modification for 20 min, however, it increased to 1.35. It appears that film surface was bombarded and surface densification occurred.

![Fig. 1. X-ray reflectivity spectra of (a) the as-deposited film (line) and (b) UV-O$_3$ treated low-k film for 20 min (dotted).](image)

Figure 2 shows the FTIR spectra of the as-deposited, annealed, and UV-O$_3$ treated samples. The intensities of all of the Si-O-Si peaks near 1030 cm$^{-1}$ increase after the treatment, while those of the SiMe$_x$ (\(x = 1, 2, \) or 3) peaks near 1260 cm$^{-1}$ decrease as the treatment time increases. This indicates that the oxygen content at the film surface increased and was accompanied by a corresponding decrease of the carbon content. The shift of the SiMe$_x$ peak from 1263 to 1268 cm$^{-1}$ also indicates that the Si bonding state changed from methyl-rich to methyl-less. The XPS analysis confirmed the increase of the oxygen concentration and the decrease of the carbon concentration at the film surface, as shown in Fig. 3. In addition, noticeable water absorption peaks are observed near 900 cm$^{-1}$ in the case of the UV-O$_3$ treated films. The water absorption peak increases with the treatment time.
Figure 2. The FTIR spectra of the UV-O₃ treated samples with SiMeₓ, Si-O-Si, -OH, SiMe₃, and SiMe₂ peaks.

Figure 3. C 1s and O 1s XPS spectra of the UV-O₃ treated samples.

Figure 4 shows the changes in the water contact angle as a function of the treatment time; the film surface changes from a hydrophobic to hydrophilic state and this is consistent with the previous FTIR spectra. The water contact angle of the as-deposited sample was 69.2° and it increased to 98.1° after the nitrogen-ambient annealing. Up to an initial modification time of 60 s, the water contact angle drastically decreases, but thereafter the change becomes more gradual. The decrease of the water contact angle means that the surface non-polar groups such as CHₓ changed to polar groups such as -O and/or -OH which strongly favor water absorption. Accordingly, a treatment time of 60 s seems to represent the transition point of UV-O₃ treatment in the system.

Figure 5a presents the high-frequency capacitance-voltage characteristics of the samples, and figure 5b summarizes the calculated dielectric constants. During the first 60 s of UV-O₃ treatment, the dielectric constant remains unchanged compared to that of the sample annealed in N₂ ambient, but it gradually increases with increasing treatment time thereafter; this is attributed to the increased cross-linking along with the elimination of the methyl groups and resultant absorption of water molecules in the film.

Figure 4. Changes in the water contact angle of the UV-O₃ modification samples.

Fig. 5. (a) The C-V traces of the as-deposited and UV-O₃ treated samples. (b) The calculated dielectric constant of the samples.
Ru deposition was performed in order to check the surface modification effects on low-\textit{k} film. In Fig. 6, SEM images show the surface morphologies of Ru films grown on the bare Si, thermal oxide, annealed low-\textit{k}, and UV-O\textsubscript{3} treated low-\textit{k} (60 s) substrates, respectively. 38 nm thick Ru (1000 cycles) films were grown on bare Si and SiO\textsubscript{2} substrates and it showed uniform and smooth morphologies. However, Ru did not make a full coverage on annealed low-\textit{k}; instead, it formed to be particles. It appears that Ru nucleation on the annealed low-\textit{k} was suppressed. Although the film showed rougher morphology than those on Si and oxide substrates, the fully-covered Ru film growth was accomplished on UV-O\textsubscript{3} treated low-\textit{k} film (60 s). The enhanced nucleation and growth of Ru on UV-O\textsubscript{3} treated low-\textit{k} film may be attributed to the structural change into SiO\textsubscript{2}-like at the film surface. A further study of the nucleation of Ru on the UV-O\textsubscript{3} treated low-\textit{k} film is currently under way.

Finally, the UV-O\textsubscript{3} surface modification process may be explained as follows. UV-O\textsubscript{3} modification decreases the thickness of low-\textit{k} film with treatment time due to highly reactive ozone, and it was confirmed by XRR and ellipsometry measurements. The treatment of excessive time adversely affects the low-\textit{k} film, increasing the dielectric constant and it is associated with the bombardments by energetic oxygen radicals and resultant water absorption. But, optimizing the treatment time as less than 60 s, the poor nucleation problem of Ru on low-\textit{k} film was solved without increasing the dielectric constant of underlying low-\textit{k} layer.

4. Conclusions

The UV-O\textsubscript{3} treatment effects on the structural and electrical properties of low-\textit{k} films were investigated. The UV-activated radical oxygen molecules removed the surface layer on top of the annealed low-\textit{k} film and it gradually modified surface layer more SiO\textsubscript{2}-like. However, this process accompanied a resultant increase in the dielectric constant, which is associated with the bombardments by energetic oxygen radicals and water absorption. The Ru suffered from the poor nucleation problem on intact annealed low-\textit{k} film. After the UV-O\textsubscript{3} treatment for the optimized treatment time of 60 s, fully-covered Ru film was obtained successfully without unaffecting the underlying low-\textit{k} film. The enhanced nucleation and growth may be attributed to the structural change of low-\textit{k} film surface.

References