Effects of N Doping in Ru-Ta on Barrier Property and Reliability Performance for Cu Interconnects

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The effects of N doping in Ru-Ta alloy on film property, barrier property against Cu diffusion and reliability performance in Cu interconnects were investigated. RuTa(N) film which was doped with N in Ru-Ta alloy was applied as a diffusion barrier layer in Cu interconnects, and barrier property and reliability performance with RuTa(N) barrier were mainly evaluated. As RuTa(N) film was annealed, N desorbed easily from RuTa(N) film due to its low thermal stability and the crystal size became larger because of the recrystallization. RuTa(N) film had the poor barrier property against Cu diffusion due to the structure of high-angle grain boundaries despite the crystal size of RuTa(N) increases and the density of grain boundaries decreases after annealing. Reliability performance of via electromigration could be improved by using Ru-Ta based alloy barrier. However, there was remarkable difference of reliability performance between RuTa and RuTa(N) barrier, and RuTa(N) had inferior reliability performance of via electromigration. On the other hand, RuTa had both good barrier property and superior reliability performance. It was found that doping N in Ru-Ta alloy degraded barrier property and reliability performance. Consequently, it is appropriate to apply RuTa single film as the diffusion barrier layer for Cu interconnects.

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Copper (Cu) interconnects have been applied to ultra large scale integrated circuits (ULSIs) to reduce the resistance of wiring and resistive-capacitance (RC) delay since the introduction of 130 nm complementary metal oxide semiconductors (CMOSs). As the feature size of trench and via continues to shrink, filling the gaps with Cu electroplating becomes more difficult. For perfectly gapped filling, the opening of trench and via after the deposition of barrier and Cu seed have to be kept far enough by thinning barrier and/or Cu seed. However, thinning Cu seed leads to Cu being agglomerated on the sidewall of both trench and via where Cu seed is too thin due to its poor coverage, resulting in the formation of voids inside trench and via. Therefore, one challenging issue for Cu interconnects is to fill the trench and via completely without the agglomeration of Cu seed on the diffusion barrier layer.

New barrier materials that have better wettability with Cu than conventional Tantalum (Ta) have been studied to achieve continuous and smooth Cu film on them. Among them, Ruthenium (Ru) has been most frequently suggested as a layer for suppressing the agglomeration of Cu seed. The barrier property against Cu diffusion of pure Ru and Ru-N is not enough. In addition, chemical mechanical polishing (CMP) process for Ru is a difficult technology and the scratch occurred during CMP process leads to the degradation of the device yield and time dependent dielectric breakdown (TDBB) reliability performance. However, Ru has the good wettability with Cu and can improve the filling property of Cu electroplating, and has another possibility in Cu interconnects such as the seed layer for direct plating onto Ru. Therefore, we focused on Ru, and Ru-based alloy was investigated as the diffusion barrier layer for Cu interconnects. As an alloy element into Ru, Ta was selected due to its good barrier property against Cu diffusion and compatibility for conventional CMP process. Ru-Ta alloy has been expected as a new barrier metal for Cu interconnects and the evaluation results of Ru-Ta alloy barrier have been reported. Generally, nitride of transition metals such as Tantalum nitride (TaN), Titanium nitride (TiN) and Tungsten nitride (W2N) have been studied as a barrier film because they have a good barrier property and they are not reactive with the wiring metal and the interlayer dielectric and the stacked barrier structure such as Ta/TaN and Ti/TiN has been applied as the barrier layer in Cu interconnects. Therefore, we focused on the RuTa(N) film which was doped with N in RuTa and RuTa/RuTa(N) stacked barrier structure for Ru-Ta alloy, and we have investigated Ru-Ta alloy as the barrier layer and reported the filling property of Cu electroplating and the reliability performance with RuTa/RuTa(N) stacked barrier structure. However, the film property of RuTa(N) and the effects of nitrogen (N) doping in Ru-Ta alloy on the device property and the reliability performance such as electromigration (EM) have not been reported.

In this paper, RuTa(N) film was applied as a diffusion barrier layer in Cu dual damascene interconnects and investigated its use as a barrier layer. The effects of N doping in Ru-Ta alloy on film property, barrier property and reliability performance are discussed.

**Experimental**

RuTa(N) film which was doped with N in RuTa was applied as a barrier layer against Cu diffusion. RuTa film was deposited by physical vapor deposition (PVD) method using Ru-Ta alloy target. The concentration of Ta in Ru-Ta alloy target was 10 at. %. N doping in RuTa was carried out by PVD processing in a mixture of argon (Ar) and N2. After the deposition of barrier film, Cu seed layer was also deposited by PVD. Then, the conventional Cu electroplating film was deposited and annealed to fill the trench and via, and the wiring was formed by removing Cu and barrier on the field with CMP process. The slurry for CMP that had been developed for pure Ru was used in this experiment.

The film resistivity of RuTa(N) was calculated with the thickness and the sheet resistance of the film measured by X-ray fluorescence (XRF) and 4-point probe, respectively. The concentration of N in RuTa(N) film was evaluated with X-ray photoelectron spectroscopy (XPS). The wettability of Cu on the barrier film was investigated by observing Cu film on the surface of the barrier layer with a scanning electron microscope (SEM) after 40 seconds of annealing at 350 C under Ar atmosphere. The crystal orientation of RuTa and RuTa(N) film was investigated by using X-ray diffraction (XRD) with characteristic X-ray CuKα radiation. The crystal size of RuTa and RuTa(N) was estimated with Scherrer’s equation.

The barrier property against Cu diffusion of RuTa single barrier, RuTa(N) single one and conventional Ta/TaN stacked one was investigated with secondary ion mass spectroscopy (SIMS) after seven hours of annealing at 350 C which was almost equivalent to the back end of the line (BEOL) process in the thermal budget. In order to establish the thermal stability of RuTa(N) film, N desorption from RuTa(N) film was investigated with thermal desorption spectroscopy (TDS).
For the evaluation of electrical property and reliability performance, a two-level Cu dual damascene structure fabricated with 45 nm node technology with chemical vapor deposition (CVD) based ultra low-k (ULK) dielectrics was used. The bottom of via was dug by the physical etching during the barrier deposition to improve the reliability performance essentially. Via resistance with RuTa single barrier, RuTa(N) single one and conventional Ta/TaN stacked one was measured with Kelvin structure. The reliability performance of EM with RuTa and RuTa(N) was evaluated and compared to that with conventional Ta/TaN. The failure analysis after EM stressed test was done with a cross sectional SEM.

Results and Discussion

Film property.—Figure 1 shows the film resistivity of RuTa(N) with the thickness of 15 nm as a function of the flow rate of N₂ to Ar. The resistivity of RuTa(N) gradually increased from $72 \, \mu\Omega \cdot \text{cm}$ to $102 \, \mu\Omega \cdot \text{cm}$ with the increase of N₂ and was saturated with the flow rate of N₂ to Ar of 3.0. In this regard, the measured value of the film resistivity included the so-called thin-film effect because this test was carried out with the thin film of 15 nm. The resistivity of TaN with the thickness of 15 nm is about $225 \, \mu\Omega \cdot \text{cm}$. It is found that the resistivity of RuTa(N) is less than half that of TaN.

Figure 2 shows the concentration of N in RuTa(N) film as a function of flow rate N₂ to Ar evaluated with XPS. The concentration of N gradually increased from 2.8 at. % to 8.0 at. % with the increase of N₂ and was saturated with the flow rate of N₂ to Ar of 3.0. This result is coincident with the result of film resistivity as shown in Figure 1, which indicates that N can be incorporated in RuTa(N) film by the deposition in a mixture of N₂ and Ar, and the concentration of N in RuTa(N) film has an influence on film resistivity.

Barrier property against Cu diffusion.—The barrier property against Cu diffusion of RuTa(N) film was evaluated with SIMS and compared to that of RuTa and conventional Ta/TaN. The samples were prepared by the deposition of Cu and each barrier films on Si blanker wafer. The thickness of Ta/TaN was 15/15 nm, and that of RuTa and RuTa(N) was 15 nm. Figure 5 shows the SIMS profiles of Cu in RuTa(N) single barrier, RuTa single one and conventional Ta/TaN stacked one after seven hours of annealing at 350 °C which is almost equivalent to the back end of the line (BEOL) process in the thermal budget. It was clear that Cu diffused into RuTa(N) barrier deeper than into RuTa and Ta/TaN. It means that the barrier property of RuTa(N) is inferior to that of RuTa.

To investigate the mechanism that the barrier property of RuTa(N) was inferior to that of RuTa, the thermal stability of RuTa(N) material
Figure 5. SIMS profiles of Cu in RuTa, RuTa(N) and Ta/TaN after annealing.

Figure 6. N intensity as a function of temperature evaluated with TDS.

Figure 7. XRD spectra of RuTa and RuTa(N) before and after annealing.

Figure 8. Mechanism of degrading barrier property of RuTa(N).

Figure 9. Schematic structure for the evaluation of electrical property and reliability performance.

was evaluated by using TDS. Figure 6 shows N intensity as a function of temperature to investigate N desorption from RuTa(N) film. Also, the result of TaN film is shown as a reference. N in TaN did not desorb even with annealing, which means that TaN is a stable material against thermal treatment. On the other hand, N in RuTa(N) desorbed at temperatures of over 240°C. This means that N is not stable in RuTa(N) and N does not form a strong bond with Ru or Ta due to the dispersion of Ta into Ru, and thus N seems to exist in non-equilibrium at RuTa grain boundaries or in RuTa grains while being deposited by PVD. The grain growth of RuTa(N) is hindered by the presence of N at the grain boundaries, resulting in the decrease of crystal size as mentioned in Figure 4.

In addition, the XRD spectra of RuTa and RuTa(N) after seven hours of annealing at 350°C was compared to that before annealing. Also, the crystal size of RuTa and RuTa(N) with FWHM of Ru(002) was estimated by Scherrer’s equation with Scherrer constant of 0.9, and the difference of crystal size after annealing between RuTa and RuTa(N) was evaluated. It is commonly known that Scherrer’s equation can be applied if there are no factors such as the stacking faults or the dislocations which have effects on the broadening of FWHM. Hence, it is not clear to use Scherrer’s equation for RuTa(N) film before annealing due to the presence of N in film. On the other hand, Scherrer’s equation can be applied for RuTa(N) film after annealing because RuTa(N) film seems to be at equilibrium after annealing due to N desorption from RuTa(N) and the recrystallization. The XRD result is shown in Figure 7. The XRD peaks of RuTa changed a little by thermal treatment and the crystal size of RuTa after annealing was estimated with 88.4 Å. On the other hand, thermal treatment made the XRD peaks of RuTa(N) intense and sharp, and the crystal size of RuTa(N) film becomes larger dramatically by annealing, which means that RuTa(N) is recrystallized by thermal treatment. The crystal size of RuTa(N) after annealing was estimated with 117.3 Å. It is found that the crystal size of RuTa(N) is much larger than that of RuTa after annealing.

Figure 8 shows the mechanism of degrading the barrier property of RuTa(N) by thermal treatment on the basis of the above understanding. The crystal size of RuTa changes little even after the thermal treatment and thus RuTa film has the structure of low-angle grain boundaries. Therefore, Cu diffusion into RuTa film is suppressed. As for RuTa(N), N in RuTa(N) film exists at RuTa grain boundaries and also in RuTa grains before annealing. As RuTa(N) film is annealed, N desorbs easily from RuTa(N) film due to its low thermal stability. The crystal size of RuTa(N) becomes larger dramatically due to the recrystallization, and thus the density of grain boundaries decreases. However, the structural regularity of grain boundaries is lowered because of N desorption, resulting in the structure of high-angle grain boundaries. Therefore, Cu diffusion into RuTa(N) film is enhanced and the barrier property of RuTa(N) is degraded despite the crystal size of RuTa(N) increases and the density of grain boundaries decreases after annealing.

Electrical property and reliability performance.—Figure 9 shows the schematic structure for the evaluation of electrical property and reliability performance. In this test, a two-level Cu dual damascene
Figure 9. Schematic structure for the evaluation of electrical property and reliability performance.

Figure 10. Cumulative probability of via resistance measured with Kelvin structure. The width of M1 trench and M2 trench are 70 nm and the diameter of V1 via is 70 nm.

structure fabricated by 45 nm node technology with CVD based ULK dielectrics was used. RuTa and RuTa(N) single barrier layer were applied to lower metal layer (M1) and upper one (M2) respectively. The conventional Ta/TaN stacked barrier layer was also applied to M1 and M2 and evaluated for reference. In addition, the physical etching process during barrier deposition for digging into the bottom of via was applied to improve the reliability performance essentially.

Figure 10 shows via resistance measured with Kelvin structure which the width of M1 trench and M2 trench are 70 nm and the diameter of V1 via is 70 nm. The via resistances with RuTa and RuTa(N) barrier were lower than that with conventional Ta/TaN stacked barrier structure. This result is attributed to the low resistivity of RuTa and RuTa(N) compared to Ta and TaN. There is no remarkable difference between RuTa and RuTa(N) barrier.

The lifetime for via EM is shown in Figure 11. The width of M1 trench is 210 nm and that of M2 trench is 70 nm. The diameter of V1 via is 70 nm. The mean time to failure (MTF) with RuTa and RuTa(N) single barrier layer was much longer than that with conventional Ta/TaN stacked one. Therefore, the reliability performance of via EM can be improved by using Ru-Ta based alloy barrier. However, there was a remarkable difference between RuTa and RuTa(N) single barrier layer, and the MTF with RuTa(N) was shorter than that with RuTa and thus EM reliability performance of RuTa(N) is inferior to that of RuTa one.

To investigate the difference of the MTF between RuTa and RuTa(N) single barrier layer, the failure analysis after EM stressed test was done. This result is shown in Figure 12. The large voids which led to the open failure formed in the upper trench both with RuTa and RuTa(N) barrier. Also, the void formed inside the via and Cu hillock formed on the sidewall of the via due to the electron flow from top to bottom with RuTa(N) barrier. Therefore, the various failures in EM test with Ru-Ta(N) barrier are observed as compared with RuTa one. This is because N doping in RuTa degrades the wettability of Cu on the barrier film or decreases the activation energy of RuTa due to the low structural regularity of grain boundaries as shown in Figure 8. It results in the difference of the MTF between RuTa and RuTa(N) barrier. Therefore, it is found that doping N in Ru-Ta alloy has a major effect on the reliability performance of via EM.

Conclusions

The effects of N doping in Ru-Ta alloy on film property, barrier property against Cu diffusion and reliability performance in Cu interconnects were investigated. N doping in RuTa degrades the wettability of Cu on the barrier layer. As RuTa(N) film was annealed, N desorbed easily from RuTa(N) film due to its low thermal stability and crystal

Figure 11. Cumulative distribution of via EM lifetime for the up-stream direction. The width of M1 trench is 210 nm and that of M2 trench is 70 nm. The diameter of V1 via is 70 nm.

Figure 12. Result of failure analysis after EM stressed test.
size became larger due to the recrystallization. RuTa(N) barrier had the poor barrier property against Cu diffusion in the BEOL process compared to RuTa one due to the structure of high-angle grain boundaries despite the crystal size of RuTa(N) increased and the density of grain boundaries decreased after annealing. The MTF of via EM with RuTa and RuTa(N) single barrier layer was longer than that with conventional Ta/TaN stacked one, and the reliability performance of via EM could be improved by using Ru-Ta based alloy. However, the MTF with RuTa(N) was shorter than that with RuTa. This is because N doping in RuTa degrades the wettablity of Cu on the barrier film or decreases the activation energy of RuTa. On the other hand, RuTa had both good barrier property and superior reliability performance. Consequently, it is appropriate to apply RuTa single film as the diffusion barrier layer for Cu interconnects.

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