The study prepared Ru/RuNₓ bilayer barriers on mesoporous SiO₂ (mp-SiO₂) dielectric layers for direct Cu electroplating applications using in situ two-step plasma-enhanced atomic chemical vapor deposition (PEALD). For the 5 nm thick Ru/RuNₓ bilayer deposited at 200 °C, obvious thermal decomposition begins at temperatures lower than 400 °C. Copper can be successfully electroplated on the as-deposited Ru/RuNₓ bilayer, and the Cu/Ru/RuNₓ/mp-SiO₂ film stack can withstand thermal treatment at temperatures up to 500 °C without significant physical and chemical degradations according to TEM and SIMS analyses. The study shows that the electroplated Cu layer behaves like a passivation layer that improves the thermal stability of the Ru/RuNₓ barrier during the thermal annealing. Pull-off tensile tests show that interfaces in the Cu/Ru/RuNₓ/mp-SiO₂ film stack have good adhesion strength, but delamination occurs at the interface between the Ru/RuNₓ bilayer and the mp-SiO₂ layer at 600 °C, resulting in Cu and Ru diffusion into the dielectric layer. The study has demonstrated that the PEALD Ru/RuNₓ bilayer structure prepared using the in situ two-step approach is suitable for the seedless Cu electroplating process in nanometer scale interconnect technology.

**Experimenal**

PEALD RuNₓ thin films were deposited on plasma-treated mp-SiO₂ thin films, which were spin-coated on 6-in. p-type Si wafers, at 200 °C using bis(ethylcyclopentadienyl) ruthenium [Ru(EtCp)₂] and a gas mixture of H₂/N₂ as the Ru precursor and the reducing reagent, respectively. The preparation of the mp-SiO₂ thin film and the pore sealing of the porous dielectric by oxygen plasma treatment have been described previously. The PEALD system had a base pressure of 5 × 10⁻⁶ Torr. One cycle of the PEALD RuNₓ deposition process consisted of four consecutive gas pulses, including the Ru(EtCp)₂ precursor injection pulse, the Ar purge pulse with a flow rate of 50 sccm, the H₂/N₂ plasma nitridation pulse, and another Ar purge pulse. During the PEALD RuNₓ deposition, the stainless steel tube containing the precursor was maintained at 75 °C to produce an adequate amount of vapor, which was carried by argon gas at a flow rate of 50 sccm. The gas line delivering Ru(EtCp)₂ was heated at 80 °C by heating tapes to prevent the precursor from condensation. For the deposition of metallic Ru thin films, an H₂ gas pulse was used instead of the H₂/N₂ pulse. Cu electroplating was carried out at room temperature using a custom plating system with an electrolyte bath comprised of H₂SO₄, CuSO₄·5H₂O and HCl. The study used a current density of 10 mA/cm² for the Cu electroplating. Thermal anneal treatment of the samples was carried out in a vacuum furnace at 10⁻³ Torr.

The surface morphology of the RuNₓ thin film was examined by scanning electron microscopy (SEM, JEOL JSM-6500 F) and atomic force microscopy (AFM, Digital Instruments, NanoScope E). The surface chemical composition was characterized by X-ray photoelectron spectroscopy (XPS, thermo VG 350) using the Mg Kα x-ray radiation. The XPS spectra presented in the report have been calibrated with the binding energy of the Pt 4f₇/₂ electron. A grazing incident angle X-ray diffraction (XRD) system (Bede D1) was used to characterize the crystallinity and the chemical phase of the PEALD and the electroplated thin films, using Cu Kα radiation with 2θ ranging from 30 to 60°. The microstructure of the Cu/Ru/RuNₓ/mp-SiO₂ film stack was studied by transmission electron microscopy.
(TEM, Philips tacnai 20). Auger electron spectroscopy (AES, thermo VG 350) and secondary ion mass spectroscopy (SIMS, Cameca ION-TOF) were used to examine the elemental distribution in the film stacks.

The adhesion strength of interfaces in the Cu/Ru/RuNₓ/mp-SiO₂ film stack was measured by the pull-off tensile test. An Al rod (2.7 mm diameter) was glued onto the Cu surface with epoxy resin and cured at 150°C for 1 h. The rod was pulled at a progressively increasing load of 0–100 kg until delamination occurred to the film stack. Electrical measurement was performed with an HP 4145B semiconductor parameter analyzer using the metal-insulator-semiconductor (MIS) capacitor measurement structure with an Al thin film sputter-deposited on the Si wafer as the backside electrode. The MIS capacitor structure has an area of 0.25 mp². The sheet resistance of the barrier layer, we deposited metallic Ru on the RuNₓ thin film using the in situ two-step PEALD process. The growth rate per cycle of the PEALD RuNₓ film increases with the point probe measurement system (Napson RT-80).

**Results and Discussion**

The PEALD RuNₓ diffusion barrier was deposited at 200°C on the oxygen-plasma treated mp-SiO₂ layer of 100 nm in thickness, which had a dense surface oxide layer and showed good dielectric properties as reported previously. The pore scaling treatment can prevent Ru precursor species from penetrating into the porous dielectric layer during the PEALD RuNₓ barrier deposition. The growth rate per cycle of the PEALD RuNₓ film increases with the Ru(EtCp)₂ pulse time and becomes saturated at about 0.038 nm/cycle when the Ru(EtCp)₂ pulse time exceeded 5 s. The saturation of the growth per cycle is characteristic for a self-limited reaction. Direct Cu electroplating could not be performed on the 4 nm thick RuNₓ thin film because RuNₓ has a high electrical resistivity. A previous study showed that a sputter-deposited RuNₓ film had a sheet resistance ten times higher than a metallic Ru thin film. To reduce the sheet resistance of the barrier layer, we deposited metallic Ru on the RuNₓ thin film using the in situ two-step PEALD process. The preparation of the Ru/RuNₓ bilayer used 90 PEALD cycles for the RuNₓ bottom layer and ten PEALD cycles for the Ru top layer. The metallic Ru layer was deposited under process conditions like the RuNₓ layer except that the H₂/N₂ mixture-gas pulse was replaced with an H₂ gas pulse. The growth rate of the PEALD Ru thin film under the process condition is about 0.03 nm/cycle according to TEM analysis.

Figure 1 shows AFM images of the mp-SiO₂ substrate before and after the deposition of the PEALD Ru/RuNₓ bilayer. The in situ two-step PEALD process produced a smooth Ru/RuNₓ bilayer barrier of good conformality. The root-mean-square (rms) surface roughness of the mesoporous silica substrate and the Ru/RuNₓ bilayer is 0.5 and 0.8 nm, respectively. The smooth surface is crucial for a seedless Cu electroplating process, which requires a continuous barrier layer of ultrathin thickness. Ruthenium nitride is thermally unstable at temperatures higher than 275°C, at which it decomposes into metallic Ru and nitrogen. The low decomposition temperature cannot meet the process temperature requirement for the Cu dual-damascene process. To evaluate the thermal stability of the PEALD Ru/RuNₓ barrier on the porous silica dielectric, we annealed the samples at various temperatures in vacuum (10⁻⁷ Torr) for 30 min, and examined the microstructure and chemical states of the annealed Ru/RuNₓ film stack. Figure 2 shows SEM images of the thermally annealed Ru/RuNₓ bilayer. When the sample is annealed at 400°C, slight film rupture occurs to the sample surface (see Fig. 2b), indicating thermal decomposition of RuNₓ has already led to film degradation. For the sample annealed at 500°C, the SEM image (Fig. 2c) shows that particles, with a size ranging from a few nanometers to one tenth of a micrometer, scatter on the sample surface. The particle growth becomes much more severe for the sample annealed at 600°C as shown by Fig. 2d. XPS and XRD analyses discussed later suggest that these particles are discrete Ru islands.

Figures 3a and 3b show the Ru(3p₃/₂) and N(1s) XPS spectra, respectively, of the Ru/RuNₓ bilayer as a function of the annealing temperature. To determine the Ru(3p₃/₂) electron energy for metallic Ru and nitrided Ru, we first performed XPS analysis separately for the as-deposited Ru and the as-deposited RuNₓ thin films. The measured Ru(3p₃/₂) energy is 462.0 and 463.0 eV for metallic Ru and nitrided Ru, respectively. Nonlinear least square curve fitting of the Ru(3p₃/₂) peak, assuming a Gaussian peak shape, shows that the

Figure 1. (Color online) AFM images of the mesoporous silica thin film before (a) and after (b) the deposition of the PEALD Ru/RuNₓ bilayer of 4 nm in thickness.

Figure 2. SEM images of (a) the as-deposited, (b) the 400°C-annealed, (c) the 500°C-annealed, and (d) the 600°C-annealed Ru/RuNₓ bilayers deposited on the mesoporous silica film.
composition of metallic Ru in the bilayer sample increases with the annealing temperature. In contrast, the N(1s) signal decreases with increasing the annealing temperature. Compared with the as-deposited bilayer, the 400°C-annealed bilayer has a larger metallic Ru composition and a smaller N(1s) signal, suggesting thermal decomposition already occurs to the underlying RuNx layer at 400°C. For the 500°C-annealed bilayer, thermal degradation is more severe as indicated by the larger decrease in the Ru(3p3/2) signal ratio of Ru to RuNₓ. The XPS result is in agreement with the SEM observation discussed above, which shows the presence of voids and particles on the annealed bilayer. The N(1s) signal of the bilayer annealed at 600°C is barely detected, indicating that RuNₓ is likely completely decomposed into metallic Ru phase.

Figure 3. (Color online) (a) Ru(3p3/2) and (b) N(1s) XPS spectra of the Ru/RuNₓ bilayer sample as a function of the annealing temperature. The two curve-fitted Ru(3p3/2) peaks at 462.0 and 463.0 eV represent metallic Ru and nitrided Ru, respectively.

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- **Figure 4**: XRD spectra of (a) the Ru/RuNₓ bilayer deposited on the mp-SiO₂ layer, and (b) the Cu/Ru/RuNₓ/mp-SiO₂ multilayer stacks as a function of the annealing temperature.

The thermal degradation of the RuNₓ layer in the bilayer structure has adverse effects on direct Cu electroplating. Under the electroplating condition of the study, Cu could be electrodeposited on the as-deposited Ru/RuNₓ bilayer, but Cu electrodeposition on a pure RuNₓ layer and the Ru/RuNₓ bilayer annealed at 400 and 500°C was unsuccessful. Noted that the 400°C-annealed Ru/RuNₓ bilayer still keeps a continuous film surface according to the SEM image in Fig. 2c. The failure in the Cu electroplating indicates that the 400°C-annealed bilayer has a significantly higher electrical resistance than the as-deposited one. It is likely that the partial thermal decomposition of the underlying RuNₓ layer at 400°C might drive nitrogen out-diffuse from the underlying RuNₓ layer into the upper metallic Ru layer, thereby increasing the sheet resistance of the bilayer structure. To ensure successful Cu electroplating, we performed the thermal treatment only after Cu was electrodeposited on the as-deposited Ru/RuNₓ bilayer. Figure 4b shows XRD spectra of a 100 nm thick Cu film electrodeposited on the Ru/RuNₓ bilayer as a function of the annealing temperature. The Cu(111) and Cu(200) peaks are the only two diffraction peaks detected in the spectra of the annealed samples, and the electroplated Cu has a high degree of the (111) texture. The preferential texture is desirable for Cu interconnects because Cu films with the (111) preferential orientation are four times better in electromigration resistance than those with the (200) orientation. The as-deposited Cu thin film has a sheet resistivity of 21.0 mΩ·cm, and the sheet resistivity of the electroplated Cu layer decreases to 14.1 mΩ·cm for all the Cu/Ru/RuNₓ film stacks annealed at temperatures between 400 and 600°C. The sheet resistivity of a thin film is an indirect indication of the crystallinity and the chemical purity of the thin film. Although, as discussed later, thermal annealing at 600°C leads to chemical and microstructure breakdowns for the Cu/Ru/RuNₓ film stack, the breakdowns result in an insignificant change in the sheet resistivity of the film stack, indicating that the barrier failure has little adverse effect on the material properties of the electroplated Cu thin film.

Figure 5 shows cross-sectional SEM images of the Cu/Ru/RuNₓ/mp-SiO₂ multilayer stack, as a function of the annealing temperature. For samples annealed at 500°C and below, the interface between the Ru/RuNₓ barrier layer and the Cu layer is free from particles and delamination (Figs. 5a and 5c). On the other hand, localized interface delamination occurs to the sample annealed at 600°C (Fig. 5d). Auger depth profiling and ESCA analyses reveal that the delamination develops at the interface between the Ru/RuNₓ barrier layer and the mp-SiO₂ layer. Figure 6 shows the Auger depth profile of the 600°C-annealed multilayer sample with the delaminated layer being mechanically removed. The depth profile clearly indicates that SiO₂ is the matrix and Ru has diffused into the mp-SiO₂ layer. Cu is also present on the surface of the separated substrate. The diffusion of Ru and Cu into the mesoporous dielectric layer can be more clearly seen in the SIMS depth profile discussed later.
Figure 5. Cross-sectional SEM images of (a) the as-prepared, (b) the 400°C-annealed, (c) the 500°C-annealed, and (d) the 600°C-annealed Cu/Ru/RuNx/mp-SiO2 multilayer stacks.

To further clarify the integrity of the interfaces in the Cu/Ru/RuNx/mp-SiO2 multilayer stack after the thermal anneal, we used TEM to examine the annealed samples. Cross-sectional TEM images of Figs. 7a and 7b clearly show that the interfaces of the Ru/RuNx barrier with the Cu layer and with the mesoporous SiO2 substrate are physically intact after the sample is annealed at temperatures below 500°C. The high resolution TEM image in Fig. 7c demonstrates that the Ru/RuNx layer in the 500°C-annealed sample is amorphous without obvious flaw, and has a uniform thickness close to that of the as-prepared multilayer stack. Unlike the bare Ru/RuNx layer, the Cu capped barrier bilayer is free from crevice and particle at the interface after the thermal anneal. For the 600°C-annealed Cu/Ru/RuNx/mp-SiO2 multilayer stack, the TEM image (Fig. 7d) shows the presence of a ~10 nm wide band of darker contrast in the surface region of the mp-SiO2 layer. The dark band is absent in the TEM images of the 400- and the 500°C-annealed samples, and it must result from Ru and Cu diffusion into the mp-SiO2 layer as shown by the Auger depth profile in Fig. 6. SIMS was also used to study if the Ru/RuNx bilayer was an effective Cu diffusion barrier at temperatures ≤500°C. Figure 8 shows SIMS depth profiles of the thermally annealed Cu/Ru/RuNx/mp-SiO2 multilayer stack. The 400- and the 500°C-annealed samples show little difference in the depth profile feature for all the analyzed elements. Noted that the Ru and N signals are entirely present in the signal regime of the mp-SiO2 layer, and the Cu signal also extends into the dielectric layer with a rapid drop at the same depth as the Ru and N signal drops. However, the signal penetration cannot represent the true elemental distribution at the interface of the ultrathin Ru/RuNx layer with the mp-SiO2 layer, but is likely a result of artifacts of the SIMS analysis, such as ion mixing and Gibbsian segregation. The concurrent and rapid drop for the Cu, Ru and N signals at the interface suggests that the Ru/RuNx barrier can effectively retard Cu diffusion into the dielectric layer at temperatures as high as 500°C. Combined with the TEM study discussed above, the SIMS analysis suggests that the electrodeposited Cu film behaves like a passivation layer that can effectively impede thermal degradation of the PEALD Ru/RuNx barrier at 500°C and below. For the multilayer stack annealed at 600°C, the profile shape of the Ru, N and Cu signals is markedly changed and the nitrogen content is greatly reduced, strongly indicating the occurrence of chemical breakdown of the barrier layer. The breakdown results in metal diffusion into the mp-SiO2 layer as revealed by the gradual signal penetration of Ru and Cu as well as the relatively high background of the Cu signal in the SiO2 region.

We performed leakage current measurements to study the effect of thermal annealing on the electrical properties of the Cu/Ru/RuNx/mp-SiO2 multilayer stack. The electroplated copper was used as the top electrode and an Al thin film sputter-deposited on the back side of the Si wafer was the bottom electrode. Figure 9 shows the leakage current density versus the electric field for the annealed multilayer samples. Prior to the thermal treatment, the multilayer sample has a leakage current density of $7.2 \times 10^{-6}$ A/cm² at the stress field of 1 MV/cm. The leakage current density slightly increases to $8.1 \times 10^{-5}$ A/cm² after the sample is annealed at 400°C. For the 500°C-annealed sample, a much larger leakage current density ($2.1 \times 10^{-5}$ A/cm²) was measured, indicating that the Ru/RuNx barrier did suffer greater thermal degradation at 500°C than at 400°C. The leakage current density of the multilayer samples annealed at ≤500°C is comparable to that of some previously reported Cu interconnect structures with an Ru based barrier. The 600°C-annealed sample has a leakage current density as high as $4.7 \times 10^{-4}$ A/cm² at
1 MV/cm, suggesting that metallic impurities may diffuse into the dielectric layer as a result of the extensive thermal breakdown of the Ru/RuNx bilayer.

Although the Ru/RuNx bilayer capped with the electroplated Cu can physically and chemically withstand the thermal anneal at temperatures as high as 500°C, the material and electrical characterizations discussed above do not provide information about the mechanical strength of the multilayer stack. We thus studied the interface adhesion of the Cu/Ru/RuNx/mp-silica multilayer stack by pull-off tensile test, and the result is shown in Fig. 10. The adhesion strength of the mp multilayer is within the range between 46 and 48 kg/cm² for samples annealed at 400 and 500°C, while the adhesion strength of the sample annealed at 600°C drastically drops to ~2 kg/cm². The adhesion strength of the Cu/Ru/RuNx/mp-SiO₂ sample annealed at temperatures ≤500°C is comparable to that of the Cu/TaNₓ/mp-SiO₂ structure reported in our previous study.²⁴ For the 400- and 500°C-annealed samples, the mechanical failure during the pull-off test takes place at the interface between the Ru/RuNx barrier layer and the electroplated Cu layer according to ESCA analysis. This is opposite to the 600°C-annealed sample, in which the delamination occurs at the interface between the barrier layer and the mp-SiO₂ layer. This adhesion test indicates the in situ two-step PEALD process can deposit an Ru/RuNx barrier layer strongly adhering to the mesoporous dielectric layer.

Conclusion

We prepared Ru/RuNx diffusion barriers on mesoporous SiO₂ thin films by PEALD for the application of seedless Cu electroplating. The 4 nm thick Ru/RuNx bilayer was deposited on the porous dielectric substrate at 200°C using the in situ two-step PEALD process. Obvious thermal degradation occurs to the bare Ru/RuNx bilayer at temperatures ≤400°C, and direct Cu electroplating is successful only on the as-deposited bilayer barrier. The electroplated Cu layer behaves like a passivation layer that can impede thermal degradation of the Ru/RuNx barrier. The Cu/Ru/RuNx/mp-SiO₂ multilayer structure can withstand the thermal treatment without significant physical and chemical degradations at temperatures ≤500°C according to TEM and SIMS analyses. The 400- and the 500°C-annealed samples have a low leakage current density. When the Cu capped multilayer sample is annealed at 600°C, thermal decomposition of the RuNx layer results in metal diffusion into the mp-SiO₂ layer and delamination at the interface between the Ru/RuNx barrier and the dielectric layer. The pull-off tensile test shows that, at temperatures ≤500°C, interfaces in the Cu/Ru/RuNx/mp-SiO₂ multilayer stack have a good adhesion strength. The study has demonstrated that the PEALD Ru/RuNx bilayer structure prepared using the in situ two-step approach is suitable for the seedless Cu electroplating process in nanometer scale interconnect technology.

Acknowledgments

This work was supported by the National Science Council of R.O.C. under Contract No. NSC97-2221-E-009-016-MY3. Technical supports from National Nano Device Laboratories is gratefully acknowledged.

National Chiao Tung University assisted in meeting the publication costs of this article.
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