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PEALD of a Ruthenium Adhesion Layer for Copper Interconnects

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Ruthenium thin films were produced by plasma-enhanced atomic layer deposition (PEALD) using an alternating supply of bis(ethylcyclopentadienyl)ruthenium $[Ru(EtCp)_2]$ and NH_3 plasma at a deposition temperature of 270°C. The film thickness per cycle was self-limited at 0.038 nm/cycle, which was thinner than the thickness obtained from the conventional ALD using oxygen instead of NH_3 plasma. The ruthenium thin film prepared with PEALD had a preferential orientation toward (002), and it was progressively promoted with NH_3 plasma power. The PEALD of ruthenium shows a merit in controlling ultrathin film thickness with less than 2 nm more precisely and more easily than the conventional ALD, due to the reduced transient period at the initial film growth stage. Also, ruthenium thin film improved the interfacial adhesion of metallorganic chemical vapor deposited copper to diffusion barrier metals by forming Cu-Ru chemical bonds at the interface without degrading the film resistivity of copper.

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With the increasing performance and packing density required in microelectronic devices, copper has been used as an interconnection metal to enhance operating speed and reliability.[1] Electrochemical plating (ECP) has now become a routine process for forming copper damascene interconnects, due to its super-filling ability, *i.e.*, it fills trenches and via holes in a bottom-up fashion without any seams or voids.[2] To realize the bottom-up filling processes, a thin and conformal copper seed-layer is required. Currently, physical vapor deposition (PVD) technique is used to deposit the seed layer. However, one challenge is to find a way to deposit a uniform seed-layer in high aspect ratio via holes and trenches of damascene structures as the feature size decreases. To overcome this technological barrier, studies have examined seedless copper damascene filling with ECP or metallorganic chemical vapor deposition (MOCVD), in which copper is deposited directly on copper diffusion barrier metals, and copper seed-layer formation using MOCVD or atomic layer deposition (ALD) have been studied.[3-5] However, the copper films fabricated using ECP, MOCVD, and ALD techniques have poor interfacial adhesion to common copper diffusion barrier metals, such as TiN, TaN, and WN, which causes failure of the copper interconnect system.[6,7] Therefore, an adequate adhesion layer for reliable adhesion is required in utilizing the seedless copper bottom-up filling techniques or preparing the copper seed-layers with MOCVD or ALD.

A ruthenium thin film prepared by ALD using bis(ethylcyclopentadienyl)ruthenium $[Ru(EtCp)_2]$ and oxygen gas was reported to have excellent performance as an adhesion layer to improve the interfacial adhesion of MOCVD copper to TiN.[8] However, the oxygen gas used as a reactant can form an interfacial metal oxide film with under-layered diffusion barrier metals, such as Ta and TaN.[9-11] This causes interconnection failure or increases via-hole contact resistance. To address this issue, we have been investigating a plasma-enhanced atomic layer deposition (PEALD) of ruthenium thin films with NH_3 plasma as a reducing agent, instead of oxygen gas. Our initial results showing that the PEALD technique enabled ruthenium film deposition, while avoiding the formation of an interfacial metal oxide, were reported recently.[12] In this paper, we present further results, including the difference in the saturated film thickness/cycle and the film growth in the transient region between the PEALD and the conventional ALD. In addition, we report that the ultrathin (~2 nm) ruthenium adhesion layer prepared by PEALD greatly improves the adhesion strength of MOCVD copper to diffusion barrier metal by forming Cu-Ru bonds.

Experimental

Ruthenium thin films were deposited on 40 nm thick TiN/100 nm thick SiO_2/Si wafers at a deposition temperature and pressure of 270°C and 3 Torr, respectively. $Ru(EtCp)_2$ and NH_3 plasma were used as the ruthenium precursor and reducing agent, respectively. $Ru(EtCp)_2$ is a liquid compound with a relatively high vapor pressure of 0.18 Torr at 80°C and good thermal stability. The $Ru(EtCp)_2$ was contained in a bubbler, which was heated at 80°C, and carried by argon gas at a flow rate of 50 sccm. To prevent precursor condensation in the feeding line, the stainless steel feeding line was heated to 90°C. One deposition cycle of ruthenium PEALD included four consecutive pulses: a pulse of $Ru(EtCp)_2$ vapor, a purge pulse with argon gas at a flow rate of 50 sccm, a pulse for NH_3 plasma exposure, and a second purge pulse with 50 sccm argon. Each purge pulse lasted for 10 s. During the NH_3 plasma pulse, NH_3 gas was introduced at a flow rate of 100 sccm mixed with 100 sccm argon. To ignite and sustain the NH_3 plasma synchronized with the deposition cycle, a rectangular shaped electrical power was applied between the upper and lower electrodes. The electrodes were capacitively coupled with a radio frequency (rf, 13.56 MHz) plasma source, operated at powers from 20 to 100 W. The lower electrode was grounded and the showerhead used to distribute the reactant gases in the reactor uniformly was used as the upper electrode. Figure 1 shows a schematic diagram of the ruthenium PEALD system. Film thickness was analyzed using field-emission scanning electron microscopy (FESEM). Film resistivity was calculated from the sheet resistance measured with a four-point probe and the film thickness. X-ray diffraction (XRD) analysis using Cu Kα radiation ($\lambda = 1.5405$ Å) was used to determine the crystal structure of the deposited films. The film density was measured using 2.4 MeV He^{2+} Rutherford backscattering spectroscopy (RBS). To evaluate the feasibility of PEALD ruthenium film as an adhesion layer for MOCVD copper films, a peel-off test using 3M Scotch tape was performed on a sample (~1 μm thick MOCVD Cu/Ru adhesion layer/40 nm thick TiN/100 nm thick thermal SiO_2 stacked on Si substrate). The MOCVD of copper was carried out for 10 min at a temperature of 180°C and a pressure of 5 Torr using hexafluoroacetylacetonate-copper-vinyltrimethylsilane $[(hfac)Cu^I(vtms)]$ as the copper precursor. The interaction between the MOCVD copper film and the PEALD ruthenium film was analyzed using X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Until now, most of the MOCVD or ALD in forming ruthenium or ruthenium oxide thin films has been utilized oxygen gas, and the

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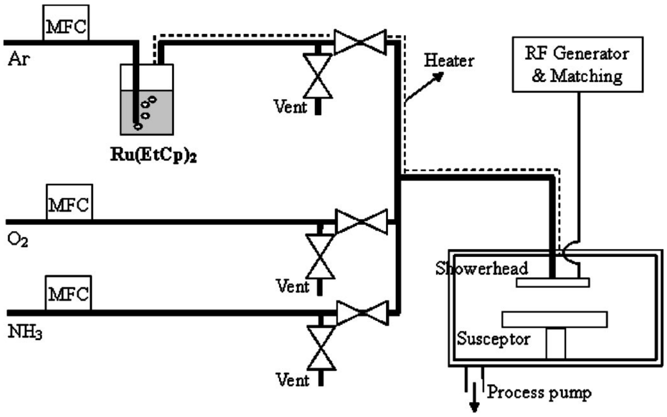

Figure 1. A schematic diagram of the deposition apparatus used in the ruthenium PEALD system.

film to be deposited was determined depending on the partial pressure of oxygen.[8,13,14] However, as mentioned before, oxygen is not a proper choice in forming ruthenium thin films which is to be applied for an adhesion layer, since oxygen has a potential to make an interfacial metal oxide layer, such as titanium or tantalum oxides, by oxidizing copper diffusion barrier metals. To avoid this problem, NH_3 plasma was used instead of oxygen. Figure 2 plots the film thickness deposited for a cycle (the film thickness/cycle) of ruthenium thin films grown by PEALD using NH_3 plasma and by conventional ALD using oxygen depending on the $Ru(EtCp)_2$ pulse time at a deposition temperature of 270°C. The pulse time of $Ru(EtCp)_2$ was varied from 2 to 10 s. The NH_3 plasma exposure time in the PEALD and the oxygen pulse time in the ALD were fixed at 10 s, respectively. In the PEALD, the film thickness/cycle increased with the $Ru(EtCp)_2$ pulse time and became saturated at about 0.038 nm/cycle when the $Ru(EtCp)_2$ pulse time exceeded 5 s, which is one of the typical characteristics of ALD, so-called a self-limited reaction. The resistivity of the ruthenium film was constant at about 12 $\mu\Omega$ cm, and was independent on the pulse time of $Ru(EtCp)_2$. These results show that NH_3 plasma successfully reduces the metal-organic precursor of $Ru(EtCp)_2$ into elementary ruthenium. It is reasonable to postulate that the lone pair of electrons in the NH_3 interacts with the ruthenium in the $Ru(EtCp)_2$ and weakens the Ru-(EtCp) bond, and that the excited species in NH_3 plasma activate the reducing reaction by making volatile compounds with the ligands in $Ru(EtCp)_2$. On the other hand, the saturated film thickness/cycle with the PEALD, 0.038 nm/cycle, was much thinner than that of the conventional ALD using oxygen, 0.15 nm/cycle. To elucidate the cause of the difference in the saturated film thickness/cycle between the PEALD and the conventional ALD, the actual number of ruthenium atoms was calculated from the film thickness/cycle and the film density measured from RBS analysis. The film density increased from 8.7 g/cm^3 in the conventional ALD to 12.03 g/cm^3 in the PEALD. The actual number of ruthenium atoms of the PEALD was less than 40% as compared to those of the conventional ALD. The calculated results are plotted in Fig. 3. The difference can be understood by adopting the concept of secondary adsorption.[15,16] During the oxygen pulse in conventional ALD, oxygen will react with $Ru(EtCp)_2$ adsorbed on the film surface and forms a new ruthenium film, and at the same time the supplementary oxygen is likely to adsorb on the newly formed ruthenium film surface. The adsorption of the supplementary oxygen is termed the secondary adsorption. As a result, the secondary adsorbed oxygen will make an additional ruthenium film to react with $Ru(EtCp)_2$ molecules supplied by the following pulse of $Ru(EtCp)_2$. The effect of secondary adsorption of oxygen was verified by removing the secondary adsorbed oxygen with hydrogen plasma. A pulse for hydrogen plasma was added after every oxygen pulses during the film deposition. In this case, the film thickness/cycle reduced drastically as compared to the ALD with oxygen only, and the actual number of ruthenium atoms formed for a cycle decreases to a similar level of PEALD, as shown by a dashed line in Fig. 3. In the ruthenium PEALD, even though NH_3 remains on the film surface after the pulse of NH_3 plasma as a result of secondary adsorption, the remained NH_3 cannot contribute to forming an additional ruthenium film, because NH_3 itself cannot decompose $Ru(EtCp)_2$ at a deposition temperature of 270°C without using plasma. These results lead to a conclusion that the absence of the effect caused from the secondary adsorption in PEALD leads to decreasing the actual number of $Ru(EtCp)_2$ molecules consumed effectively to constitute ruthenium film in a cycle. As a consequence, the saturated film thickness/cycle of PEALD reduces as compared to that of the conventional ALD of ruthenium.

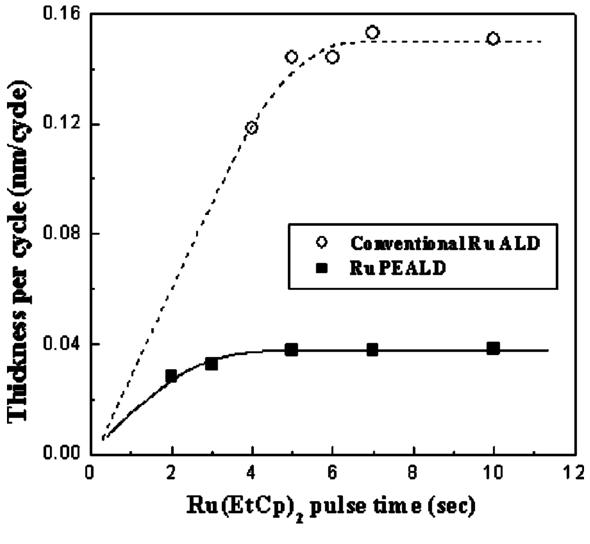

Figure 2. The dependence of the thickness/cycle of ruthenium thin films grown by PEALD using NH_3 plasma and conventional ALD using oxygen on the $Ru(EtCp)_2$ pulse time. The pulse time of $Ru(EtCp)_2$ was varied from 2 to 10 s. The NH_3 plasma exposure time in the PEALD and the oxygen pulse time in ALD time were fixed at 10 s, respectively.

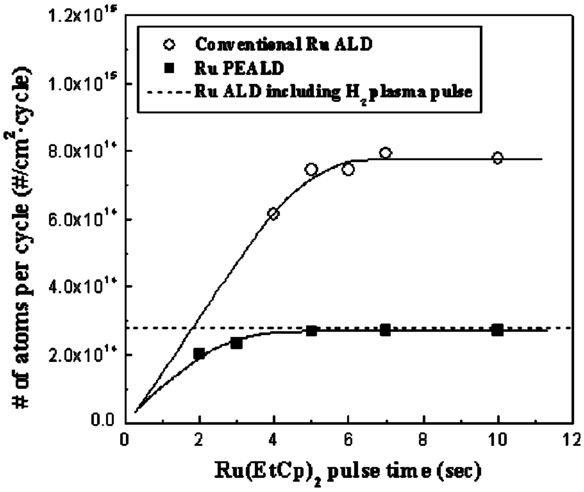

Figure 3. The number of ruthenium atoms/cycle, which calculated from the thickness/cycle and the film density measured by RBS analysis, in the PEALD and conventional ALD.

Figure 4a depicts the dependence of the film thickness/cycle on plasma pulse time and power. At a plasma power of 100 W, the film

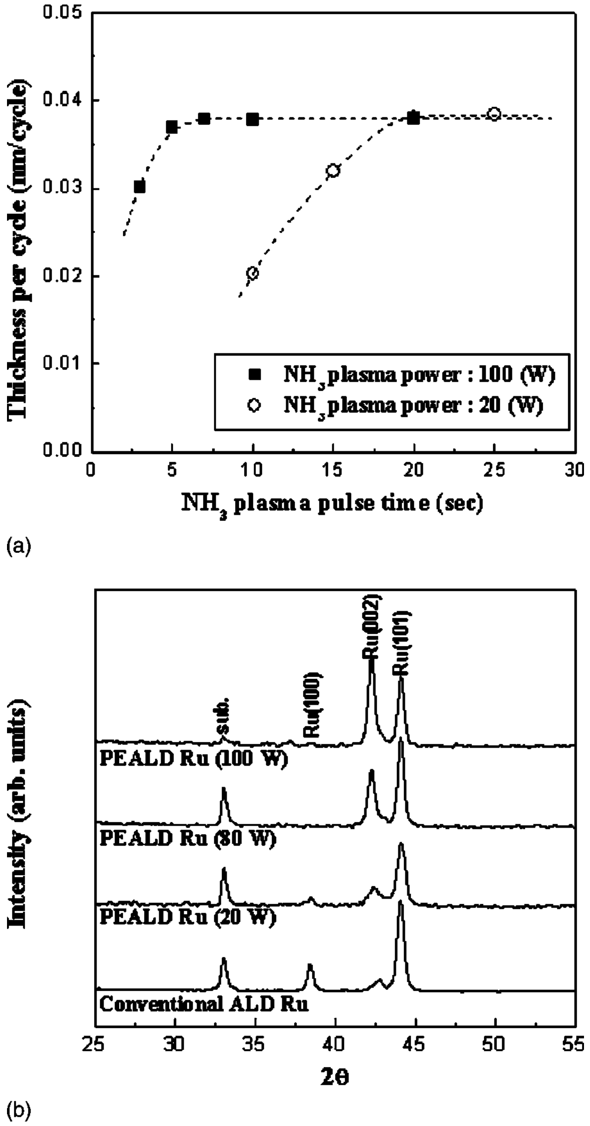

Figure 4. (a) Dependence of the film thickness/cycle on plasma pulse time for plasma power of 100 and 20 W. (b) XRD patterns obtained from the ruthenium films grown by PEALD and conventional ALD.

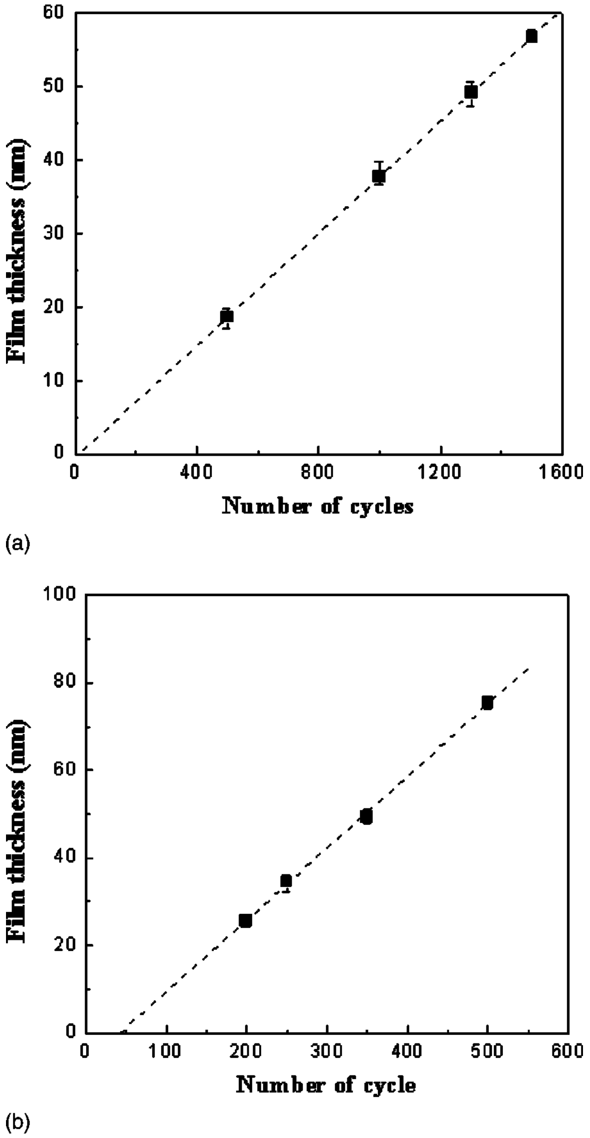

Figure 5. Thickness of ruthenium films as a function of deposition cycles in (a) the PEALD and (b) the conventional ALD.

thickness/cycle was saturated when the plasma pulse time exceeded 5 s. That is, a 5 s NH_3 plasma pulse is sufficient to completely achieve the reduction of adsorbed $Ru(EtCp)_2$. When the plasma power was decreased to 20 W, the plasma pulse time to complete the reduction reaction elongated to 20 s. Figure 4b shows the XRD patterns obtained from ruthenium films prepared with PEALD and ALD. In the ruthenium film prepared by the ALD with oxygen, it was preferentially oriented to (101). But, the preferred orientation of the film prepared by the PEALD with NH_3 plasma was changed from (101) to (002) with increasing NH_3 plasma power. This implies that the additional energy supplied by NH_3 plasma enhances the rearrangement of ruthenium atoms to the orientation of (002), the most thermodynamically stable face in a hexagonal close-packed (hcp) crystal structure.

In Fig. 5, the ruthenium film thickness is plotted against the number of deposition cycles for the PEALD and ALD. As expected, the film thickness increased linearly with the number of deposition cycles, regardless of the PEALD and ALD. However, the extrapolated line did not pass through the origin, and it intercepted on *x*-axis with a perceptible positive value especially for the case of the conventional ALD. This means there exits an extended period having lower growth rate in the early stage of the film growth in the conventional ALD. Generally, this early stage is called as transient region. Aaltonen reported a similar behavior with a long transient region in the ruthenium ALD using oxygen,[14] and insists that the film growth retards until abundant ruthenium nuclei are formed, since the dissociative adsorption of oxygen, which leads the oxidative decomposition of adsorbed $Ru(EtCp)_2$, is probably facilitated on ruthenium nuclei than on the original substrate surface. On the contrary, in ruthenium PEALD, the energetic reducing agent of NH_3 plasma can directly decompose the adsorbed ruthenium precursor without having a dependence on the substrate surface. Thus, a longer transient region is appeared on the ALD using oxygen than on the PEALD using NH_3 plasma. In a previous paper, we reported that the ruthenium film deposited by the PEALD has an improved surface roughness as compared with that prepared by the conventional ALD.[12] From the above analysis, it is expected that the absence of transient region in the PEALD makes the ruthenium film have a smoother surface than the film prepared by the ALD. Also, the film smoothness will be helpful to form a continuous and ultrathin (<2 nm) ruthenium film.

Table I. Results of adhesion test of 1 μm thick MOCVD copper.

Cycles	None	20 cycle	40 cycle	60 cycle	80 cycle
Thickness of Ru adhesion layer	—	0.73 nm	1.11 nm	1.88 nm	2.64 nm
Results of adhesion test	Fail	Fail	76% Pass	100% Pass	100% Pass

To evaluate the feasibility of PEALD ruthenium thin films as an adhesion layer to improve the interfacial adhesion of MOCVD copper to copper diffusion barrier metals, a peel-off adhesion test using Scotch tape was performed after MOCVD of about 1 μm thick copper on a ruthenium adhesion layer. Before the scotch tape peel-off test, the crossed grid with 2 mm intervals was scratched on the specimen with a cutter to quantitatively analyze the adhesion property, so that the results of the adhesion test are expressed as the ratio of number of the remained grids after adhesion test to the total number of grids. Because the adhesion layer should be as thin as possible, we carried out adhesion tests while progressively decreasing the thickness of ruthenium layer. A 2 nm thick ruthenium adhesion layer is sufficient to improve the interfacial adhesion of MOCVD copper to the diffusion barrier metals without any failure in the peel-off adhesion test, as summarized in Table I. To determine the mechanism responsible for the increased adhesion strength, XPS analysis was performed. As shown in Fig. 6, the copper atoms at the interface between copper and ruthenium are electronically perturbed with respect to the bulk copper atoms, and shift towards a lower binding energy in the Cu $2p_{3/2}$ XPS spectra, while Cu $2p_{3/2}$ XPS spectra of interface copper on TiN is not shifted. These results indicate that a chemical interaction between Cu and Ru is anticipated at the interface and, therefore, the interfacial adhesion of MOCVD copper to the diffusion barrier metal is improved.

For a given adhesion layer, there is a trade-off between stability and adhesion performance with copper. That is, if a thin film layer does not react with copper at all, it may exhibit excellent stability, but poor adhesion. Conversely, if the layer reacts too easily with copper, it may degrade the performance of the copper interconnect, such as by increasing the resistance of the copper layer, despite exhibiting excellent adhesion. Therefore, in addition to its adhesion properties, stability with the copper layer is important for utilizing ruthenium thin films as an adhesion layer. To verify the stability of ruthenium with a copper layer, the sheet resistance of a copper layer deposited on a ruthenium adhesion layer has been investigated before and after a heat treatment. Heat-treatment was carried out using a rapid thermal process (RTP) at a temperature of 450°C for 1 h in argon ambient. The sheet resistance of the copper layer is not changed after the heat-treatment, as ruthenium is immiscible with copper thermodynamically. Therefore, ruthenium films grown by PEALD can be used as an effective adhesion layer between MOCVD copper and copper diffusion barrier metals.

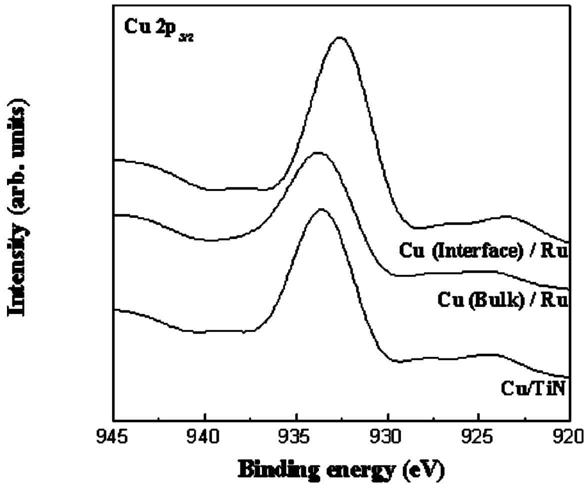

Figure 6. XPS analysis of MOCVD copper on ruthenium and TiN.

Conclusions

Ruthenium thin films were successfully deposited by PEALD using $Ru(EtCp)_2$ and NH_3 plasma at 270°C. NH_3 plasma acted as an effective reducing agent for $Ru(EtCp)_2$. The ruthenium film formed during one deposition cycle was saturated at 0.038 nm/cycle, and its resistivity was 12 μΩ cm. The decrease in the film thickness/cycle compared with conventional ALD was attributed to film densification and the decrease in the number of atoms deposited per cycle due to the absence of the effect caused from the secondary adsorption in PEALD. The preferred orientation of the PEALD ruthenium film was changed from the (101) peak to the (002) peak with increasing NH_3 plasma power. The transient region at the early stage of film growth was even shorter in PEALD than in conventional ALD, which facilitates the precise thickness control of ultrathin films. A peel-off adhesion test confirmed that an ultrathin ruthenium adhesion layer prepared by PEALD greatly improved the interfacial adhesion of MOCVD copper to TiN barrier metal. The formation of localized Cu-Ru chemical bonds at the interface enhances adhesion. Therefore, a PEALD ruthenium thin film can be effectively utilized as an adhesion layer.

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References

1. S. P. Murarka, *Mater. Sci. Eng., R.*, **19**, 87 (1997).
2. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Dev.*, **42**, 567 (1998).
3. O. K. Kwon, J. H. Kim, H. S. Park, and S. W. Kang, *Electrochem. Solid-State Lett.*, **6**, C109 (2003).
4. R. Kröger, M. Eizenberg, D. Cong, N. Yoshida, L. Y. Chen, S. Ranaswami, and D. Carl, *J. Electrochem. Soc.*, **146**, 3248 (1999).
5. R. Solanki and B. Pathangey, *Electrochem. Solid-State Lett.*, **3**, 479 (2000).
6. A. Furuyama, N. Hosoi, and Y. Ohsihita, *J. Appl. Phys.*, **78**, 5989 (1995).
7. T. Hara and K. Sakata, *Electrochem. Solid-State Lett.*, **4**, G77 (2001).
8. O. K. Kwon, J. H. Kim, H. S. Park, and S. W. Kang, *J. Electrochem. Soc.*, **151**, G109 (2004).
9. Z. Wang, H. Sakaue, S. Shingubara, and T. Takahagi, *Jpn. J. Appl. Phys., Part 1*, **42**, 1843 (2003).
10. H. J. Sun, K. M. Kim, Y. Kim, K. J. Cho, K. S. Park, J. M. Lee, and J. S. Roh, *Jpn. J. Appl. Phys., Part 1*, **42**, 582 (2003).
11. H. G. Tompkins and J. A. Sellers, *J. Vac. Sci. Technol. A*, **12**, 2446 (1994).
12. O. K. Kwon, S. H. Kwon, H. S. Park, and S. W. Kang, *Electrochem. Solid-State Lett.*, **7**, C46 (2004).
13. S. E. Park, H. M. Kim, K. B. Kim, and S. H. Min, *Thin Solid Films*, **341**, 52 (1999).
14. T. Aaltonen, P. Alén, M. Ritala, and M. Leskelä, *Chem. Vap. Deposition*, **9**, 45 (2003).
15. W. S. Jeon, S. Yang, C. S. Lee, and S. W. Kang, *J. Electrochem. Soc.*, **149**, C306 (2002).
16. J. W. Lim, H. S. Park, and S. W. Kang, *J. Appl. Phys.*, **88**, 6327 (2000).