

Application of Pulsed Chemical Vapor Deposited Tungsten Thin Film as a Nucleation Layer for Ultrahigh Aspect Ratio Tungsten-Plug Fill Process

Byeonghyeon Jang and Soo-Hyun Kim[†]

School of Materials Science and Engineering, Yeungnam University 280 Daehak-ro, Gyeongsan, Gyeongbuk 38541, Republic of Korea

(Received June 24, 2016 : Revised August 10, 2016 : Accepted August 10, 2016)

Abstract Tungsten (W) thin film was deposited at 400 °C using pulsed chemical vapor deposition (pulsed CVD); film was then evaluated as a nucleation layer for W-plug deposition at the contact, with an ultrahigh aspect ratio of about 14~15 (top opening diameter: 240~250 nm, bottom diameter: 98~100 nm) for dynamic random access memory. The deposition stage of pulsed CVD has four steps resulting in one deposition cycle: (1) Reaction of WF₆ with SiH₄. (2) Inert gas purge. (3) SiH₄ exposure without WF₆ supply. (4) Inert gas purge while conventional CVD consists of the continuous reaction of WF₆ and SiH₄. The pulsed CVD-W film showed better conformality at contacts compared to that of conventional CVD-W nucleation layer. It was found that resistivities of films deposited by pulsed CVD were closely related with the phases formed and with the microstructure, as characterized by the grain size. A lower contact resistance was obtained by using pulsed CVD-W film as a nucleation layer compared to that of the conventional CVD-W nucleation layer, even though the former has a higher resistivity (~100 μΩ·cm) than that of the latter (~25 μΩ·cm). The plan-view scanning electron microscopy images after focused ion beam milling showed that the lower contact resistance of the pulsed CVD-W based W-plug fill scheme was mainly due to its better plug filling capability.

Key words tungsten(W), pulsed chemical vapor deposition, W-plug, nucleation layer, contact resistance.

1. Introduction

Chemical vapor deposited(CVD) tungsten(W) has been widely used to fill small contact and via holes with a high-aspect-ratio(HAR) in multilevel metallization of ultra-large-scale-integrated(ULSI) devices.¹⁾ The traditional W-plug deposition consists of three steps; silane (SiH₄) pretreatment, W nucleation, and W-plug fill.²⁻⁴⁾ Prior to SiH₄ pretreatment, Ti/TiN is typically deposited as contact and glue/barrier layer. A SiH₄ pretreatment is used to make a homogeneous and fast nucleation of W film on TiN.⁵⁾ In addition, the SiH₄ pretreatment could enhance the barrier performance of TiN by stuffing the grain boundaries with Si or SiH_x.⁶⁾ The SiH₄ pretreatment is followed by the nucleation process, which traditionally involves the reduction of tungsten hexafluoride (WF₆) by SiH₄. The use of SiH₄ in nucleation step ensures a fast nucleation and

deposition of W on TiN with little incubation time and prevents the reaction of WF₆ with Si or with the Ti contact layer. The third step, plug fill, is accomplished using H₂ reduction of WF₆. H₂ is used for W-filling instead of SiH₄ in order to give a conformal film with the lowest possible resistivity and particle levels.

It is generally accepted that the deposition of W nucleation layer using SiH₄ reduction is a critical step in W-plug deposition because its conformality is relatively poor as compared to H₂ reduction of WF₆. For example, it shows adequate step coverages for larger features (> 80 % with opening diameters > 0.13 μm, 5:1 AR) but starts to degrade for narrower and higher-aspect-ratio features.⁷⁾ Moreover, the requirement for W-plug deposition for ever-shrinking semiconductor devices described by international technology roadmap for semiconductors places more stringent demands on plug fill.⁸⁾ In this respect, atomic

[†]Corresponding author
E-Mail : soohyun@ynu.ac.kr (S.-H. Kim, Yeungnam Univ.)

© Materials Research Society of Korea, All rights reserved.

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

layer deposition(ALD)⁹ is one of the most promising techniques to fulfill the above requirement. ALD-W films were deposited using disilane (Si_2H_6),¹⁰ SiH_4 ,^{7,11-13} and diborane (B_2H_6)¹³ as reducing agents of WF_6 . Excellent step coverages at the HAR contact and via were obtained using ALD process. However, an ideally very low growth rate of 1 monolayer of W (~ 0.25 nm) per cycle¹⁰ as compared to that by conventional CVD can limit its applications in the semiconductor processing. In addition, the requirement of new deposition equipment for ALD process is another burden from the economical viewpoint.

Previously, we have reported the modified CVD-W nucleation process, called by pulsed CVD.^{14,15} Here, pulsed CVD is composed of 4 steps, resulting one deposition cycle: (1) Reaction of WF_6 with SiH_4 . (2) Inert gas purge. (3) SiH_4 exposure without WF_6 supply. (4) Inert gas purge while the conventional CVD is consisted of the continuous reaction of WF_6 and SiH_4 . By using this process, we could obtain a W nucleation layer with an excellent conformality at the HAR contact holes while still preserving a higher growth rate than that of conventional ALD. In this paper, we investigate the integration of pulsed CVD-W films as nucleation layers for W-plug deposition at DRAM technology. In this paper, the plug filling characteristics and contact resistance with pulsed CVD-W film as a nucleation layer were investigated and compared with conventional CVD-W nucleation process.

2. Experimental Procedure

Fig. 1 shows the schematic diagram of the sequence of pulsed CVD. The deposition stage of pulsed CVD is composed of 4 steps, resulting one deposition cycle: (1) Reaction of WF_6 with SiH_4 . (2) Inert gas purge. (3) SiH_4 exposure without WF_6 supply. (4) Inert gas purge. In other cases, H_2 could be added in the first and the third step. One of the stronger advantages of this process is the ability to use current CVD tools (Applied Materials Centura 5200 WxZ cold-walled and single wafer chamber) and process to successfully fill the ultrahigh aspect ratio contacts and vias. Detailed deposition conditions for pulsed CVD-W films were summarized in Table 1. For comparison, conventional CVD W films were deposited at a pressure of 30 Torr and susceptor temperature of 400 °C with 10 standard cubic centimeter per minute (sccm) of SiH_4 and 50 sccm of WF_6 gases diluted in Ar.

In order to study the plug-filling characteristics and electrical properties, Si wafers were processed through DRAM process flow. The contacts connecting Al metal line with W bit line were patterned using ArF lithography and etched using high-density plasma. Then, to remove the thin oxide layer and surface etch damage, a deglaze

Table 1. Summary of deposition conditions for pulsed CVD-W films.

	Sample I	Sample II
1 st step	WF_6 : 30 sccm SiH_4 : 10 sccm	WF_6 : 30 sccm SiH_4 : 10 sccm H_2 : 1000 sccm
2 nd step	Ar/ N_2 purge	Ar/ N_2 purge
3 rd step	SiH_4 : 35 sccm	SiH_4 : 35 sccm H_2 : 1000 sccm
4 th step	Ar/ N_2 purge	Ar/ N_2 purge

Table 2. Summary of contact dimensions used in this study, which was determined by FIB-XTEM. Aspect ratio was determined by the ratio of height and top diameter of contact.

	Contact height (μm)	Top diameter (nm)	Bottom diameter (nm)	Aspect ratio
Contact A	3.53	240	98	14.7
Contact B	3.53	255	110	13.8

step with 300:1 buffered oxide etchant(BOE) was carried out prior to Ti/TiN deposition. Ti glue layer was deposited into the contact by a biased ionized metal plasma(IMP) sputtering.¹⁶ And then, without breaking vacuum in an Applied Materials Endura chamber, 10-nm-thick TiN was deposited at 450 °C by thermal decomposition of tetrakis-(dimethylamido) titanium [TDMAT, $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$] with two periodic plasma densification steps for every 5 nm growth. Following the TiN deposition, W-plug process was performed. Blanket W deposition and etch-back were used to fill the contacts followed by metal line deposition. Here, W-plug deposition was composed of SiH_4 pretreatment, pulsed CVD-W deposition as a nucleation layer, and W-plug fill at the deposition temperature of 400 °C using the same chamber. Finally, metal line patterning was accomplished. Contact resistances were measured using contact chain structures with two different contact sizes. Table 2 summarizes the contact dimensions used in this study. Contact filling characteristics after W-plug deposition were characterized by plan-view scanning electron microscopy(SEM) operated at accelerating voltage of 200 kV(HD2000) after focused ion beam(FIB) cutting.

3. Results and Discussion

The systematic investigations on the properties of pulsed CVD-W films with deposition conditions have been described in details elsewhere.^{14,15} Here, we will point out the important findings. The pulsed CVD-W film had a much lower roughness (~ 0.7 nm at the thickness of ~ 20 nm) and better conformality at HAR contacts (AR: $\sim 14:1$, top opening diameter: ~ 250 nm, and bottom diameter: ~ 100 nm) as compared to that of conventional CVD-W nucleation layer deposited using

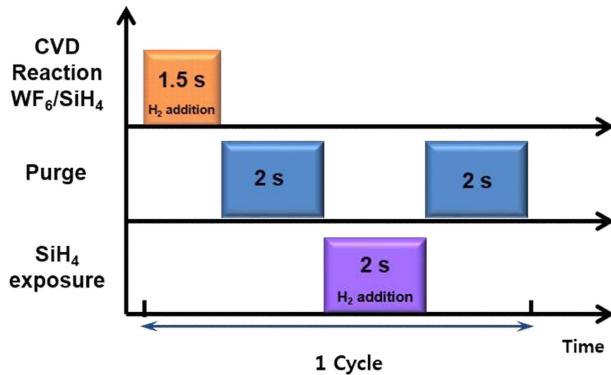


Fig. 1. Schematic diagram of pulsed CVD process.

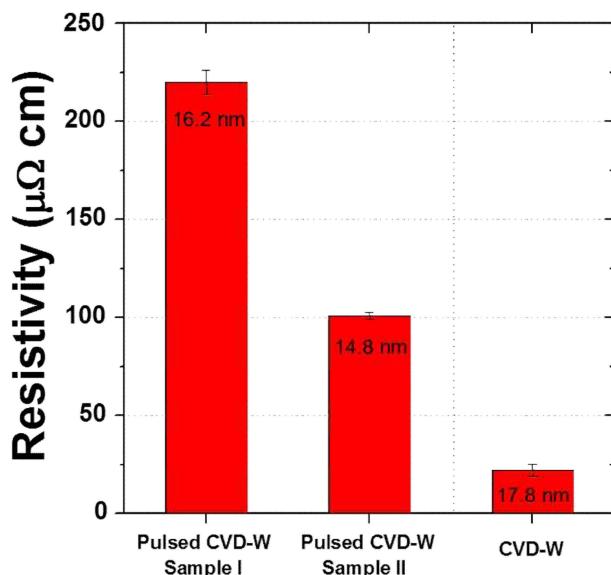


Fig. 2. The resistivities of pulsed CVD-W films with deposition conditions; $T_{dep.} = 400$ °C.

WF₆ and SiH₄ as shown by Fig. 1.

Fig. 2 shows the resistivities of pulsed CVD-W films. It was found that film resistivities deposited by pulsed CVD were closely related with phases formed and microstructure characterized by grain size. For the sample I, the resistivity is as high as ~210 $\mu\Omega\text{-cm}$. The high resistivity of sample I might be due to small grain size ranging from 5 to 11 nm and the formation of β -W phase with higher resistivity as compared to that of body centered cubic α -W. β -W films are reported to have significantly higher resistivity, as much as 150~350 $\mu\Omega\text{-cm}$ ¹⁷ while α -W films deposited by CVD typically have a resistivity of ~20 $\mu\Omega\text{-cm}$. H₂ addition into the first and the third step (sample II) increased the grain size (11~18 nm) and prevented the film from forming an A15 β -W phase with a high resistivity, resulting in a film resistivity of ~100 $\mu\Omega\text{-cm}$ (Fig. 2). But, it is still higher than that of conventional CVD-W nucleation layer (~25

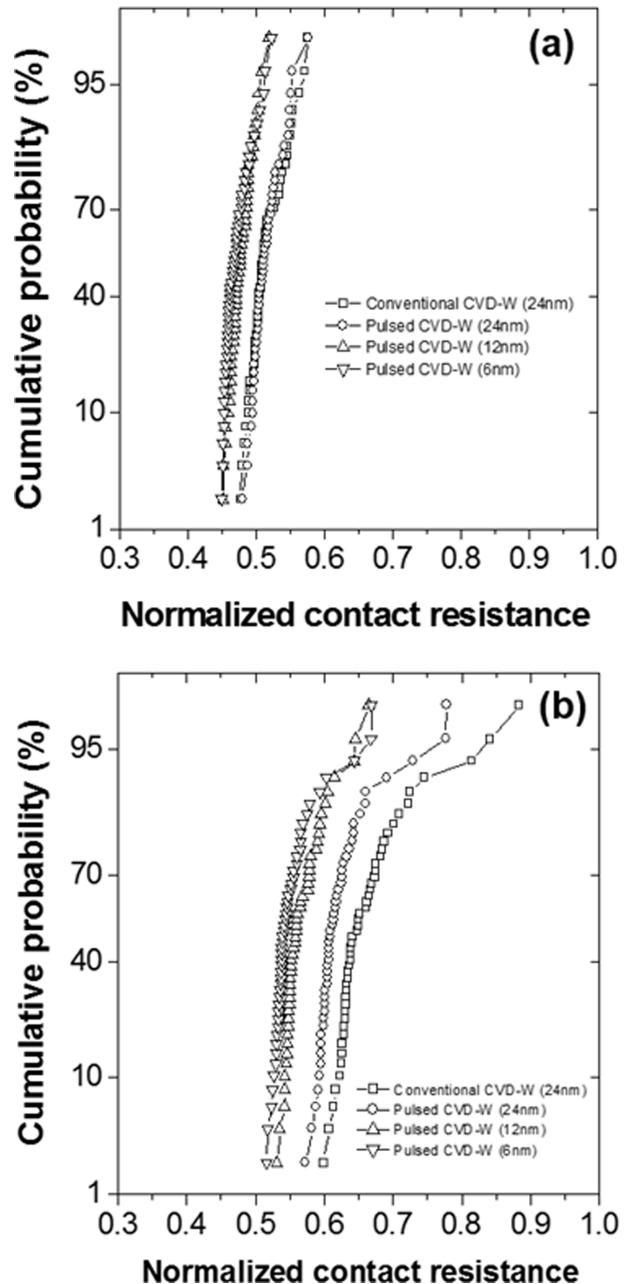


Fig. 3. The distribution of normalized contact resistances at the contact chains connecting Al metal line with W bit line; (a) contact chain A and (b) contact chain B. Corresponding contact dimensions are summarized in Table 2.

$\mu\Omega\text{-cm}$).

Fig. 3 shows the contact resistance distribution at the contact chains with different contact sizes. For contact chain A (Fig. 3(a)), a new scheme of pulsed CVD-W nucleation layer/W-plug fill shows a similar contact resistance compared with that of a conventional scheme of CVD-W nucleation layer/W-plug fill with the same thicknesses of nucleation layers. Considering a much higher resistivity of pulsed CVD-W nucleation layer, Fig.

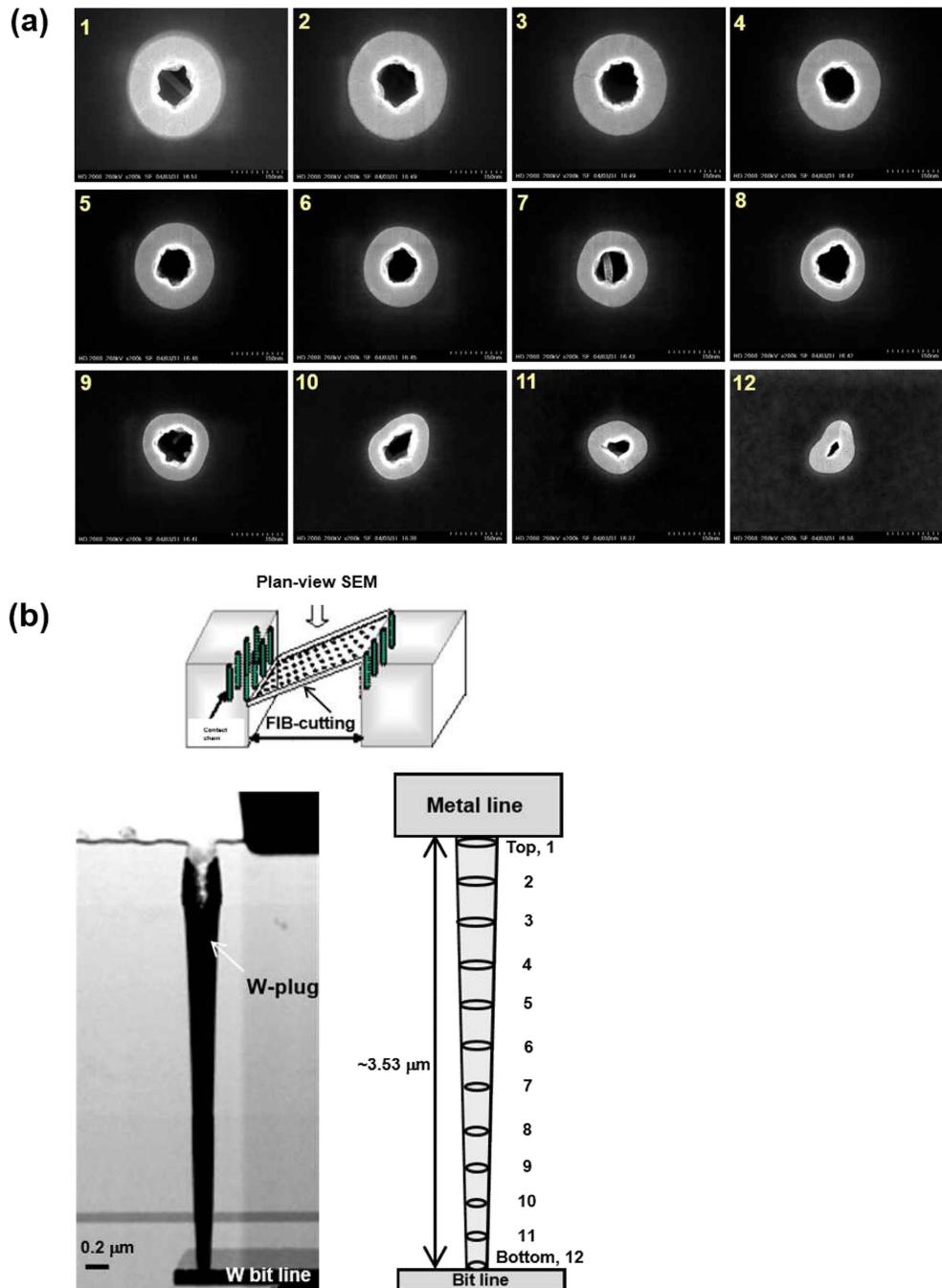


Fig. 4. (a) The Plan-view SEM images of conventional CVD-W nucleation layer/W-plug fill scheme at contact chain B with contact depths and (b) the schematic diagram for sample preparation using FIB-cutting and typical FIB-XTEM image showing contact filling. 1 marked in the Fig. 5(a) indicates the plug filling at the top of contact and 12 that at the bottom of contact.

3(a) indicates that the plug filling capability of the new W-plug scheme will be better compared to the conventional one. Fig. 3(a) also shows that the contact resistance decreases as the thickness of pulsed CVD-W film decreases. This is both due to the decrease in cross-sectional area occupied by pulsed CVD-W film with a high resistivity ($\sim 100 \mu\Omega\text{-cm}$) and the increase of cross-sectional area occupied by low-resistivity plug fill film ($\sim 15 \mu\Omega\text{-cm}$).

The minimum thickness evaluated as a nucleation layer in this study was as thin as $\sim 6 \text{ nm}$ and the successful integration of this ultrathin nucleation layer indicates that pulsed CVD provides uniform nucleation and accurate thickness control like ALD process.

As the contact size decreases (Fig. 3(b)), the new W-plug scheme of pulsed CVD-W nucleation layer/W-plug fill shows a contact resistance lower than that of con-

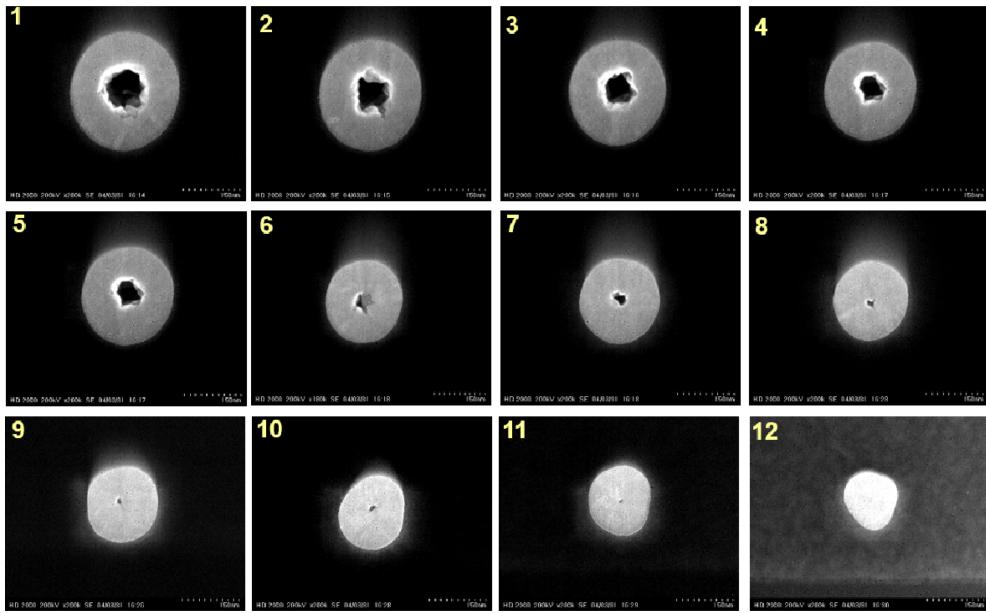


Fig. 5. The Plan-view SEM images of pulsed CVD-W nucleation layer (sample II)/W-plug fill scheme at contact chain B with contact depths.

ventional W-plug scheme even though the nucleation layers with the same thicknesses were applied. This indicates that the plug filling capability of conventional W-plug scheme is deteriorated with the reduction in feature size while the new one preserves its good filling capability. Fig. 3(b) also shows that the contact resistance can be lowered with a thinner nucleation layer, which is the same results with the case of larger size contact. Thus, it could be concluded that the pulsed CVD-W based plug fill scheme has a clear advantage with the reduction in device size.

Fig. 4(a) shows the plan-view SEM images of conventional W-plug scheme at contact chain B (see Table 2) after W-plug deposition. Twelve images were taken through the contact depths after precise cutting using FIB and thus, number 1 marked in the SEM image indicates the plug filling at the top of contact and 12 that at the bottom of contact. In Fig. 4(b), a schematic diagram for sample preparation and a typical FIB-XTEM image showing contact filling are provided. This technique is found to be successfully used for clearly observing the plug filling with contact depth at the very HAR contacts and vias even though the cross-sectional view observation fails to characterize the plug filing. As can be seen in Fig. 4(a), the conventional scheme has a large seam and this seam is formed through the bottom of contact. However, the drastically improved plug-filling capability of the new W-plug scheme is demonstrated as shown by Fig. 5. It is clear that the size of the seam at the same contact depth is significantly reduced and it disappears at the middle of contact. In the case of the new W-plug

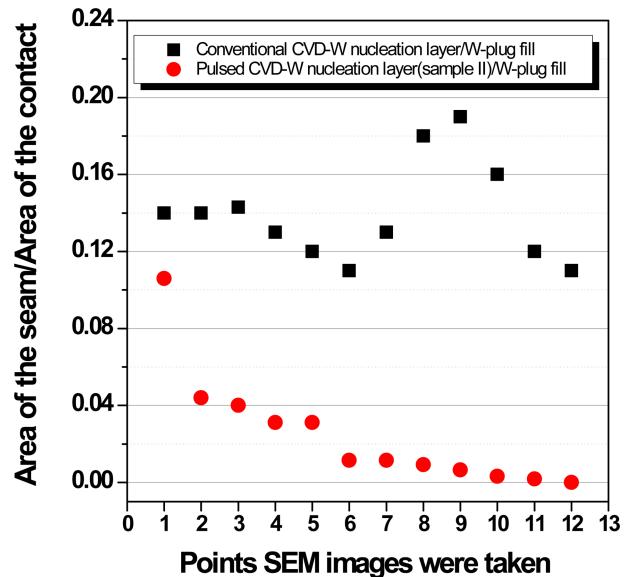


Fig. 6. The ratio of the area of the seam formed in the contact versus the cross-sectional area of the contact as a function of the contact depth, which was calculated considering Fig. 4(a) and Fig. 5. In fact, the x-axis of the graph indicated the points SEM images were taken, which was shown at Fig. 4(b).

scheme, the seam in W-plug is mainly due to bowed contact profile not the conformality of nucleation layer. Fig. 6 showed the ratios of the area of the seam formed in the contact versus the cross-sectional area of the contact as a function of the contact depth [in fact, the positions SEM images were taken, which was shown at Fig. 4(b)] with W nucleation layer process schemes,

based on Fig. 4(a) and Fig. 5. As expected, the ratio was always higher for the W-plug formed by a conventional CVD-W nucleation process/W-plug fill irrespective of the contact depth as compared to that for the one by a new W-plug process using a pulsed CVD nucleation layer (sample II). It was already reported that the step coverage of the pulsed CVD-W nucleation layer was superior to that of the conventional CVD-W nucleation layer.¹⁴⁾ And, from Fig. 6, it is apparent that the improved step coverage of the nucleation layer resulted in the improved W-plug film. Thus, it can be deduced that a lower contact resistance of the new W-plug scheme of pulsed CVD-W nucleation/W-plug fill is mainly due to the excellent filling capability at the very small-sized contacts considering the most of contact was consisted of the W-plug fill not the nucleation layer.

In the case of W-CVD using SiH₄-chemistry, it is well known that the step coverage of W film is mainly degraded by the decrease of SiH₄ concentration at a deep contact hole due to its lower diffusion coefficient and higher reaction order as compared to H₂-chemistry.¹⁾ As can be seen in Fig. 4(a), the poor step coverage of nucleation layer could lead to a large seam in the final plug fill. This may become open after subsequent planarization processing such as etch-back or chemical mechanical polishing, which increases the contact and via resistance and degrades the quality of contact and via. However, in the case of pulsed CVD, both purge step using inert gas and SiH₄ exposure step provided sequentially after a short CVD reaction prevented the reactant starvation at HAR contact hole, resulting in improving the film conformality. Moreover, the addition of H₂ in the precursor pulsing and reactant pulsing step (sample II) could improve the step coverage of pulsed CVD-W film further. The improved conformality of nucleation layer leads to the excellent W-plug filling.

5. Summary and Conclusions

In summary, thin and conformal W nucleation layer is critically necessary for successfully filling the ultrahigh-aspect-ratio small plug as the device is ever-shrinking. In this study, we have demonstrated the new W-plug integration scheme to use pulsed CVD-W film as a nucleation layer. Pulsed CVD process has a strong advantage that it successfully fills the HAR contacts and vias using the current CVD tools. The results showed that pulsed CVD-W based plug fill scheme showed a lower resistance at the contact holes of DRAM as compared to conventional CVD-W based one. A novel characterization technique using FIB cutting clearly showed that a drastically improved plug filling was achieved by employing pulsed CVD-W film. Improved filling was thought to be due to

the excellent step coverage of nucleation layer deposited by pulsed CVD. One of important findings in this study is that the pulsed CVD-W based plug fill scheme has a clear advantage due to its better plug-filling capability as the contact dimension is reduced. Thus, it could be concluded that pulsed CVD-W process can be considered as one of the possible solutions to deposit a very thin W nucleation layer for future DRAM W-plug process.

Acknowledgments

This study(2015R1A2A2A04004945) was supported by the Mid-career Researcher Program through NRF grant funded by the MEST and also partially supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea(NRF-2014H1C1-A1066809).

References

1. J. E. J. Schmitz, Chemical vapor deposition of tungsten and tungsten silicide, Noyes, Park Ridge, New Jersey (1992).
2. E. K. Broadbent and C. L. Ramiller, *J. Electrochem. Soc.*, **131**, 1427 (1984).
3. C. M. McConica and K. Krishnamani, *J. Electrochem. Soc.*, **133**, 2542 (1986).
4. E. J. McInerney, T. W. Mountsier, B. L. Chin and E. K. Broadbent, *J. Vac. Sci. Technol.*, **B11**, 734 (1993).
5. S. B. Herner, S. A. Desai, A. Nak, and S. G. Ghanayem, *Electrochem. Solid-State Lett.*, **2**, 398 (1999).
6. M. A. Nicolet, *Appl. Surf. Sci.*, **91**, 269 (1995).
7. T. Omstead, G. Chris D'Couto, S.-H. Lee, P. Wongsenkaum, J. Collins and K. Levy, *Solid State Technol.*, **51**, 45 (2002).
8. International Technology Roadmap for Semiconductors (ITRS), 2011 Edition, Interconnect Summary.
9. T. Suntola, *Handbook of Crystal Growth*, edited by D. T. J. Hurle, (Elsevier Science B. V., 1994), Vol. 3, Chapter 14.
10. J. W. Klaus, S. J. Ferro and S. M. George, *Thin Solid Films*, **360**, 145 (2000).
11. S.-H. Lee, L. Gonzalez, J. Collins, K. Ashitani and K. Levy, *Conference Proceedings ULSI XVII*, 649 Materials Research Society (2002).
12. K. Okubo, H. Ishizuka, K. Suzuki, K. Sato and M. Tachibana, *Conference Proceedings ULSI XVII*, 661 Materials Research Society (2002).
13. M. Yang, H. Chung, A. Yoon, H. Fang, A. Zhang, C. Knepfler, R. Jackson, J. S. Byun, A. Mak, M. Eizenberg, M. Xi, M. Kori and A. K. Sinha, *Conference Proceedings ULSI XVI*, 655 Materials Research Society (2002).
14. S.-H. Kim, E.-S. Hwang, S.-Y. Han, I.-H. Lee, S.-H. Pyi, N.-J. Kwak, H. Sohn and J. Kim, *Electrochem. Solid-*

State Lett., **7**, G195 (2004).

15. S.-H. Kim, E.-S. Hwang, S-C. Ha, S.-H. Pyi, H.-J. Sun, J.-W. Lee, N. Kawk, J.-K. Kim, H. Sohn and J. Kim, J. Electrochem. Soc., **152**, C408 (2005).

16. Y. Tanaka, E. Kim, J. Forster and Z. Xu, J. Vac. Sci. Technol., **B17**, 416 (1999).

17. P. M. Petroff, A. K. Sinha, T. T. sheng, H. J. Levinstein and F. B. Alexander, J. Appl. Phys., **44**, 2545 (1973).