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At the edge between metal organic chemical vapor deposition and atomic layer deposition: Fast Atomic Sequential Technique, for high throughput conformal deposition

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A comparison of the metal organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), and a new deposition method, the Fast Atomic Sequential Technique (FAST®), was completed. Within all the materials which can be deposited by the FAST technique, the case study of TiN thin film deposition by reaction of tetrakis(diethylamino)titanium precursor with NH_3 reactant gas is presented here. The thickness and resistivity measurements revealed that while the FAST deposition is five times faster than the ALD, the lowest resistivity achieved is four times lower than MOCVD minimum resistivity, thus equivalent to ALD at 100 $\mu\Omega$ cm. Moreover, a 25% gain toward lower action energy of the FAST deposition compared to the MOCVD tends to support a different reaction mechanism between the two techniques. Additionally, the FAST technique introduces new process parameters offering the possibility to change the deposition technique to either a MOCVD-like or to an ALD-like deposition in the same tool, thus allowing to choose between high throughput and high conformality or for a compromise of the two. Then, using high aspect ratio vias, the higher conformality of FAST compared to MOCVD is shown. Evolution of the conformality on different aspect ratios devices shows that while ALD is conformal whatever the aspect ratio, MOCVD is not suitable for vias with an aspect ratio higher than 5:1, whereas FAST can achieve a conformality higher than 60% in aspect ratios of 35:1. © *2016 American Vacuum Society.* [http://dx.doi.org/10.1116/1.4942497]

I. INTRODUCTION

For the last three decades,[1] atomic layer deposition (ALD) is investigated as a possible replacement of the CVD techniques, when thin layers, precise control of the thickness, and good conformality are required.[1–3] High volume manufacturing of CMOS is using ALD since the 90 nm node for some of the layers thinner than 10 nm, mainly for oxide but also for some of the nitride materials.[4] One of the limitations of the ALD technique is the requirement of a chemistry adapted to its principle, i.e., based on two halves' reactions. Such a chemistry is not available for every materials,[5,6] even if a lot of research groups are working on the development of new precursors.[5,6] The second drawback, highly limiting ALD's adoption in the industry, is the low growth rate (from 0.5 to 5 Å per cycle, a cycle being several tens of seconds, for the metal nitride deposition[6–8]), resulting in a low throughput for thin layers and dissuasive process time for layers thicker than 20 nm.

The other chemical deposition technique available, the metal organic chemical vapor deposition (MOCVD), on the other hand, is not suited for thin layers due to its high growth rate, making the precise control of the deposited thickness difficult if not impossible in the case of layers thinner than 50 nm. Furthermore, the MOCVD technique was proven not to be adapted for conformal deposition in high aspect ratio structures.[9] When used on structures with aspect ratio higher than 10:1, the conformality is dropping down to 20% or less.[9–11]

The in-house developed Fast Atomic Sequential Technique (FAST) introduced here is based on a MOCVD reactor with a dual-channel showerhead and ALD valves for pulsing the reactant gas and the precursor. These specifications allow to obtain a conformal deposition in high aspect ratio structures, with high deposition rates. The FAST was already used for deposition of Al_2O_3 from trimethylaluminium and O_2 plasma, ZnO from diethylzinc and O_2 plasma, TiO_2 from tetrakis(diethylamino)titanium (TDEAT) and O_2 plasma, TiN from TDEAT and NH_3, TaN from tert-butylimino-tris(diethylamido)tantalum and NH_3, and finally for SiO_2 and SiN from tetraethyl orthosilicate and O_2 plasma or NH_3, respectively. Other materials are also under investigation. In this article, the advantages of the FAST compared to the well documented MOCVD and ALD techniques are illustrated with the case of thin TiN films.

II. EXPERIMENT

TiN thin films were deposited on 200 mm Si wafers, with a 100 nm SiO_2 layer for resistivity measurements and with vias of aspect ratio from 1:1 and up to 35:1 for conformality observation. All the depositions were done in the same deposition chamber using the same process parameters (temperature, pressure, flow ratio,…), and only the injection scheme was changed. A description of the injection schemes used is given in the next paragraph. TiN was deposited using TDEAT precursor and NH_3 reactant gas. TDEAT is a liquid precursor, carried to a vaporizer with He vector gas (Direct Liquid Injection system). When not specified, the temperature of the sample was 360 °C during deposition process.

The concentrations of precursor and reactant gas in the chamber, depending on the technique used for deposition, are presented in arbitrary unit (Fig. 1). In graph (a), the flow and thus the concentration are constant in the MOCVD mode, and both precursor and reactant gas are introduced into the chamber at the same time. In graph (b), in the ALD technique, precursor and reactant gas pulses are separated by a purge of the chamber to exhaust the deposition reaction by-products and the unreacted reagents. In graph (c), in the FAST, precursor and reactant gas are pulsed into the chamber, without any purge in-between. In the FAST mode, the pulses of precursor and reactant gas can be adjusted to have either MOCVD-like (by increasing the pulse length and introducing overlapping of the pulses, graph d) or ALD-like (by increasing the idle time between the pulses) deposition. All intermediaries' positions between CVD and ALD can be achieved with the proper tuning of the FAST parameters.

The thickness of the deposited layers was measured with an ellipsometer on full sheet wafers and with a SEM in the profile of via (top, middle, and bottom observations), and the resistivity was measured by the four point probe resistivity technique. The thickness and resistivity measurements were done on 20 points, and the calculated nonuniformity was used for the error bars shown in Figs. 2 and 3.

III. RESULTS AND DISCUSSION

A. TiN thin film characterizations

In Fig. 2 is presented the thickness evolution depending on the process time of the three techniques described previously: MOCVD, ALD, and FAST.

It appears that, after a 12 s nucleation delay, the MOCVD growth rate is steadily increasing until it reaches a linear
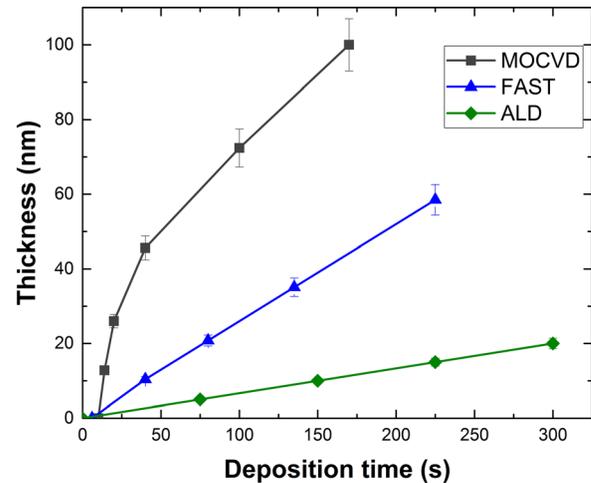

FIG. 2. (Color online) Variation of the TiN deposited thickness with process time and deposition technique.

regime, after about 50 nm of the deposited material. The growth rate in this linear regime is 5 Å s^{-1}. A similar growth rate was already reported for MOCVD deposited TiN.[12,13]

On the other hand, the ALD technique presents no or little nucleation delay and a linear regime is observed from the first cycle of deposition. This linear growth from the first few nanometers can be explained by the principle of the ALD, i.e., the surface saturation deposition mode leading to a deposition limited to atomic layer at each cycle. The extracted growth rate of the ALD is 0.6 Å s^{-1}, value in line with the growth rates reported in the literature.[6,14]

In between these two techniques is the FAST, with no or little nucleation delay, and a linear growth of 2.7 Å s^{-1}, steady state growth is reached already after the first few nanometers of deposited material. Using different pulsation
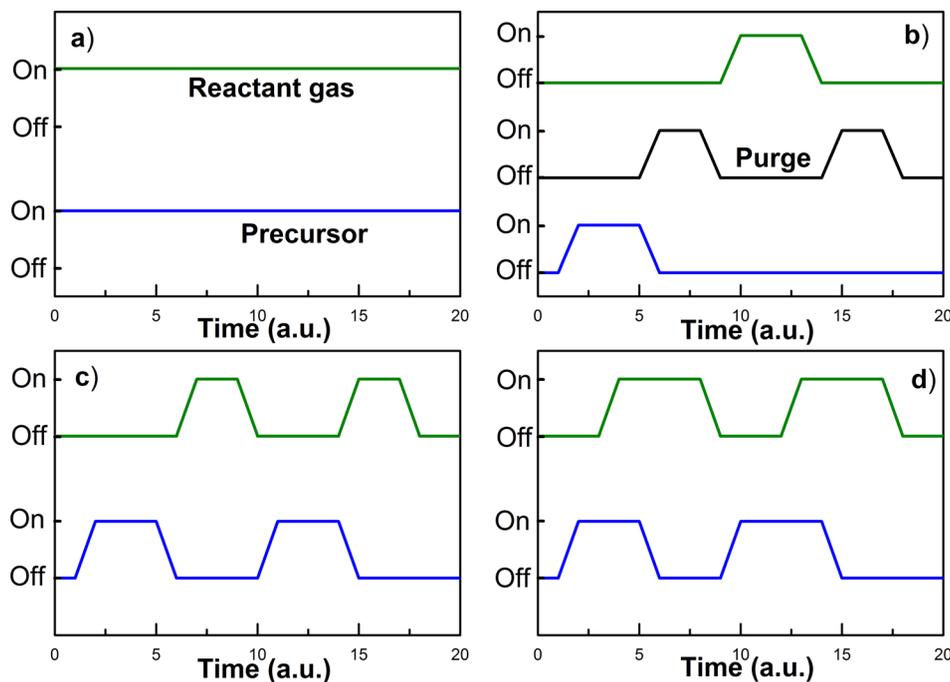

FIG. 1. (Color online) Precursor and reactant gas concentration profile depending on the technique used. (a) MOCVD, (b) ALD, (c) FAST, and (d) example of MOCVD-like FAST.
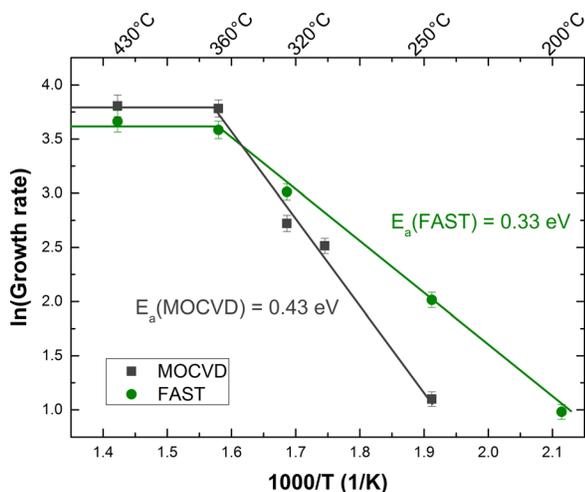
FIG. 3. (Color online) Arrhenius plot of the MOCVD and FAST growth rates.

FIG. 4. (Color online) Variation of the resistivity with TiN thickness increase for the three deposition techniques.

scheme in the FAST has a great influence on the growth rate. To obtain a MOCVD-like deposition, the pulse duration and the pulses overlap of both the precursor and reactant gas have to be increased [as presented Fig. 1(d)], in that case the growth rate will increase toward the MOCVD growth rate. To obtain an ALD-like deposition, the pulse duration has to be reduced while the idle time between pulses has to be increased; by doing so, the FAST deposition will be controlled by surface saturation phenomenon, as for ALD.

In Fig. 3 is plotted the logarithm of the MOCVD and FAST growth rates, depending on the inverse of the temperature, in order to calculate the activation energy of the deposition reaction based on the Arrhenius law.[15]

Figure 3 reveals a 25% lower activation energy of the FAST compared to the MOCVD. This lower activation energy indicates that the reaction between the precursor and the reactant gas requires less energy to take place, i.e., the FAST is more favorable for the deposition of TiN than the MOCVD. Such difference can be explained by the separation of the precursor and the reactant gas, which are not pulsed at the same time on the wafer surface. This separation allows a better exhaust of the reaction by-products, in turn leading to a higher number of nucleation sites available, finally resulting in an enhanced growth of the layer.

It is important to highlight that the lowest deposition temperature achieved with the MOCVD is 250 °C, below this temperature only a monolayer is observed at the surface of the sample, and there is not enough energy to activate the nucleation sites and thus to allow a continuous growth of the layer. Yet, for the FAST deposition, the lowest deposition temperature is 200 °C, close to the ALD minimum deposition temperature of 180 °C; this further supports the advantages of the FAST, with the better parts of both MOCVD and ALD.

About 360 °C, the kinetic of the deposition reaches a plateau where the MOCVD growth rate is superior to the FAST one. This lower growth rate of the FAST can be explained by the lower amount of precursor and reactant gas enterin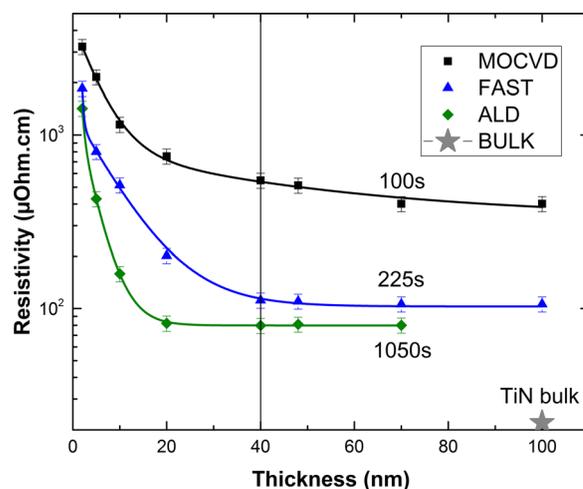g into the deposition chamber. However, it is important to notice that even though the amount of reactants used in the case of FAST is half the amount used in the MOCVD, the growth rate is only 15% lower for the FAST deposition. This difference suggests a higher efficiency of the FAST compared to the MOCVD.

Finally, the resistivity of the TiN layers was compared for the three techniques: MOCVD, ALD, and FAST. The variation of the resistivity with the layer's thickness is presented in Fig. 4.

For comparison, the resistivity of bulk TiN (Ref. 16) is also presented in Fig. 4, at 22 $\mu\Omega$ cm. The layers deposited by MOCVD stabilize on a resistivity plateau at 400 $\mu\Omega$ cm, with a layer thickness of 50 nm or more. Similar resistivity for the TiN MOCVD deposited from TDEAT and NH_3 can be found in the literature.[13,17] Due to the different reaction mechanism taking place during the ALD, lower resistivity of the TiN layer can be achieved. As seen from Fig. 4, with the ALD, only 17 nm of TiN are needed to reach the resistivity plateau located at 80 $\mu\Omega$ cm, resistivity conform to the data found in the literature.[6,18] Finally, using the FAST, a minimum resistivity of 100 $\mu\Omega$ cm is achieved with only 24 nm of TiN. As for the growth rate, FAST is a compromise between ALD and MOCVD and appears to be closer to ALD in the case of the resistivity characteristics of the deposited layer.

One can notice that the resistivity is decreasing with the increase in thickness of the layer. An explanation to this variation is the increasing influence of oxygen in the material as the film thickness decreases. Part of this oxygen originates from the initial growth of TiN on SiO_2 substrate. It was already shown that the first molecules of TDEAT precursor absorbed on the sample must react with the OH-groups from the surface, and as a consequence, the first monolayer mainly contains metal–oxygen bonds.[19] The percentage of the Ti–O bonds in the film increases with decreasing film thickness and can reach, for example, 30% in a 0.65 nm thick TiN layer. Thirty percent represents one monolayer of Ti–O in a three-monolayer structure. Moreover, oxidation is also observed at the surface of the sample due to the vacuum

break.[20] From literature data,[21] the resistivity of TiO_x (x < 2) is known to be about $3.10^3 \mu\Omega$ cm; hence, the thinner is the layer, the higher is the relative oxidation and the higher is the resistivity.

In addition to the resistivity variation with the thickness, Fig. 4 reveals that whereas layers deposited by FAST and ALD have a low resistivity; the MOCVD layer is four times more resistive than these. One can suppose that the separation of the precursor and reactant gas pulses allows to minimize the amount of reaction by-products kept in the material. Moreover, it was already reported that resistivity is highly impacted by the presence of reaction by-products in the layer.[13] This effect is further supporting the decrease in the activation energy, introduced earlier, when comparing FAST to MOCVD.

Overall, it appears that the TiN deposited from TDEAT and NH_3 using the FAST has similar properties as the TiN deposited by ALD, whereas the FAST throughput is closer to the MOCVD process than to the ALD process.

B. Conformality investigation

Vias etched in Si wafer were used to investigate the conformality of the MOCVD, ALD, and FAST techniques. Figures 5(a)–5(c) are presenting the SEM observation of a 20 nm TiN layer in 35:1 vias deposited by MOCVD, ALD, and FAST, respectively.

It is well known that the MOCVD technique is not suitable for vias with an aspect ratio higher than about 10:1,[9] in 35:1 vias the conformality is hardly reaching 20%, Fig. 5(a). At the opposite end, ALD conformality, in Fig. 5(b), is reaching 100%, thanks to the principle of the technique, i.e., the alternative surface saturations. Thus, no matter the aspect ratio of the via, by tuning the pulse lengths, it will always be possible to deposit a layer with a conformality higher than 90% with ALD. Using the FAST, with the pulses schematic given in Fig. 1(c), the conformality of the layer is close to 60%. Nevertheless, by adapting the precursor and reactant gas pulses duration, position, and overlap, it is possible,
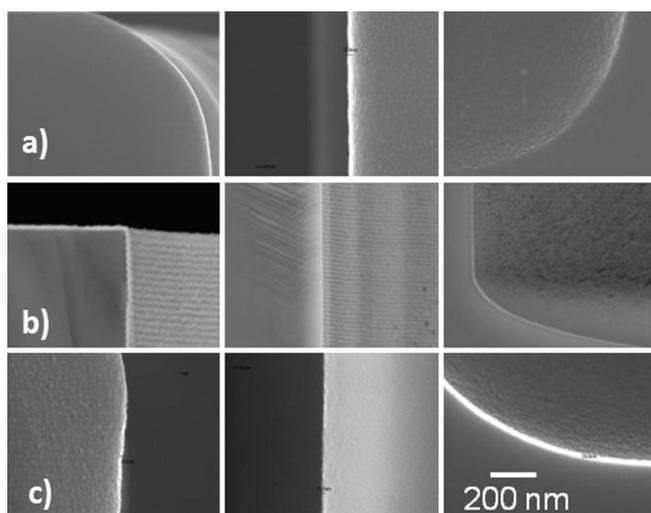
using the FAST, to obtain a process and a conformality similar to the ALD technique but with a higher throughput.

In Fig. 6 is presented the conformality evolution of a 20 nm TiN layer deposited by MOCVD, ALD, and FAST, in vias with aspect ratio ranging from 1:1 to 35:1.

As introduced earlier, the ALD technique allows, at the cost of a long process time, to reach a conformality close to 100% whatever the aspect ratio of the vias, here up to 35:1.

Thanks to the introduction of new process parameters, the FAST can be adapted to obtain the required characteristics of the layer, i.e., one can choose either a high growth rate at the cost of a lower conformality, a limited growth rate but allowing high conformality or an optimal conformality with a production compatible growth rate.

IV. SUMMARY AND CONCLUSION

In this article, the example of TiN thin film deposition was used to demonstrate the advantages of the FAST. Compared to the MOCVD, FAST permits to reduce the deposition rate, for a better control of the layer thickness, reduces the activation energy by 25% of the deposition reaction, and allows to deposit a layer with four times lower resistivity. Moreover, the FAST enhances the conformality of the deposited layer in high aspect ratio vias, resulting in a 60% conformality in 35:1 aspect ratio vias. When compared to ALD, the FAST reduces the process time by a factor four, without losing some of the benefits of the ALD. Thus, the thickness control of the layer is precise down to the nanometer and the resistivity of the layer remains similar.

Thanks to the introduction of new process parameters, the pulse position and the pulse overlay, the FAST appears to be the most flexible of the three techniques compared in this article. Furthermore, the FAST permits to choose either a MOCVD-like deposition, either an ALD-like deposition, allowing coverage of all the gap between the MOCVD and the ALD techniques. And as mentioned earlier, all the layers presented in this article deposited by MOCVD, ALD, and FAST were obtained using only one deposition chamber.

FIG. 5. Conformality of a 20 nm TiN layer deposited by (a) MOCVD, (b) ALD, and (c) FAST techniques on 35:1 aspect ratio vias.
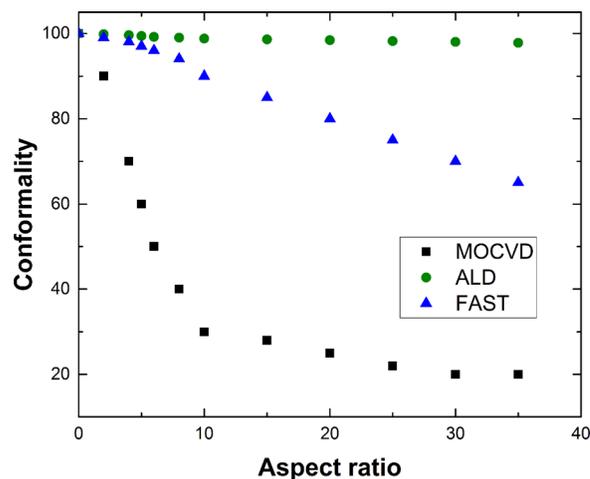

FIG. 6. (Color online) Evolution of the conformality of a 20 nm TiN layer deposited on increasing aspect ratio vias by MOCVD, ALD, and FAST.

In order to fully comprehend the differences of reaction mechanism between the MOCVD, ALD, and FAST, an investigation of the reaction by-products will be carried out using a residual gas analyzer. Based on the results, it will be possible to propose the adequate chemical reaction of each technique.

ACKNOWLEDGMENTS

[1]R. L. Puurunen, Chem. Vap. Deposition **20**, 332 (2014).
[2]R. W. Johnson, A. Hultqvist, and S. F. Bent, Mater. Today **17**, 236 (2014).
[3]H. H. Gatzen, V. Saile, and J. Leuthold, *Micro and Nano Fabrication: Tools and Processes* (Springer, Berlin/Heidelberg, 2015).
[4]T. Kääriäinen, D. Cameron, M. L. Kääriäinen, and A. Sherman, *Atomic Layer Deposition: Principles, Characteristics, and Nanotechnology Applications* (Wiley, Hoboken, NJ, 2013).
[5]M. Leskelä and M. Ritala, Angew. Chem. Int. Ed. **42**, 5548 (2003).
[6]M. Leskelä and M. Ritala, Thin Solid Films **409**, 138 (2002).
[7]J.-Y. J. Y. Kim, G. G.-H. H. Choi, Y. Y. Do Kim, and H. Jeon, Jpn. J. Appl. Phys. **42**, 4245 (2003).
[8]F. Piallat *et al*., Microelectron. Eng. **107**, 156 (2013).
[9]T. Gupta, *Copper Interconnect Technology* (Springer, New York, 2010).
[10]S. Y. No, J. H. Oh, C. B. Jeon, M. Schindler, C. S. Hwang, and H. J. Kim, J. Electrochem. Soc. **152**, C435 (2005).
[11]G. Ruhl, M. Krenzer, and J.-M. Batke, *Proceedings of IEEE/SEMI Advanced Semiconductor Manufacturing Conference* (2009), p. 33.
[12]J. Lee, J. Kim, and H. Shin, Thin Solid Films **320**, 15 (1998).
[13]J.-Y. Yun, S.-W. Rhee, S. Park, and J.-G. Lee, J. Vac. Sci. Technol., A **18**, 2822 (2000).
[14]J.-W. Lim, H.-S. Park, and S.-W. Kang, J. Electrochem. Soc. **148**, C403 (2001).
[15]S. Arrhenius, Z. Phys. Chem. **31**, 197 (1899).
[16]MatWeb, "Material property data," http://www.matweb.com/ (2015).
[17]S. W. Kim, H. Jimba, A. Sekiguchi, O. Okada, and N. Hosokawa, Appl. Surf. Sci. **100-101**, 546 (1996).
[18]G. Cho and S.-W. Rhee, ECS J. Solid State Sci. Technol. **3**, P185 (2014).
[19]F. Volpi, L. Cadix, G. Berthomé, E. Blanquet, N. Jourdan, J. Torres, and G. Berthom, Microelectron. Eng. **85**, 2068 (2008).
[20]H. G. Tompkins, J. Appl. Phys. **70**, 3876 (1991).
[21]M. D. Banus, T. B. Reed, and A. J. Strauss, Phys. Rev. B **5**, 2775 (1972).