Atomic Layer Deposition of W- based layers on SiO_2

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Abstract—**W<Si> and $W_{1-x}N_x$, where x= 15- 22 at%, thin films were grown using the ALD (Atomic Layer Deposition) principle. Growth rate of W<Si> films is about 4- 5 monolayers/ cycle at 300- 350 ºC. Growth rate of $W_{1-x}N_x$ is 0.5 monolayer/cycle at 325- 350 ºC. Standard Deviation (STDV) of thickness is about 2% for 20nm layers. Specific resistivity is 180 mW cm for W<Si> and as low as 220-340 mW cm for $W_{1-x}N_x$ 20nm films. 4 point probe sheet resistivity test is applied to Cu/ Barrier/ SiO_2 stacks with ramping temperature. No changes of normalized resistance reflecting Cu-Barrier interaction was measured after 500 ºC annealing cycle.**

Keywords— **Atomic Layer Deposition; tungsten; copper metallization; diffusion barrier; tungsten nitride.**

I. INTRODUCTION

Diffusion barriers are required in silicon IC's with Cu interconnects to protect Si and dielectrics against Cu-diffusion and Cu against diffusion of Si [1]. There are some major geometrical and physical requirements for barriers. First of all, the thickness of the diffusion barrier should be 10 nm in 2004 and 5 nm in 2010, according to International Technology Roadmap. The conventional ionised Physical Vapour Deposition (iPVD) is unable to deposit such a thin layer conformally over features with high aspect ratio. The Atomic Layer Deposition (ALD) method, based on the chemisorption of gas- precursors, allows to decrease the growth rate down to =1 monolayer/ cycle and to deposit films with 100% step coverage. References in the literature about ALD of W- based films on dielectrics are scarce, although $W_xN_yC_{1-x-y}$ films grown by ALD have been reported to be promising barriers referring to low resistance and morphology [2]. Clearly, more research should be done in this field for understanding of the growth mechanism of the layers.

II. EXPERIMENTAL PROCEDURE

A. ALD equipment

Deposition experiments are carried out in ALD-system. The Si-wafer is placed on a Mo- susceptor in a load- lock. When the load- lock is pumped down to $1*10^{-5}$ mbar, the Mo- susceptor is transferred into a hot reactor and placed on the bottom heater. The bottom heater goes up forming a closed hot- wall reactor. The reactor volume is 24 ml. The base pressure in the reactor is $2.7* 10^{-7}$ mbar.

B. Wafer preparation and deposition experiments

Prior the deposition, wafers with 700nm thermal oxide grown in water vapor were cleaned with a standard cleaning in fuming nitric acid and boiling 69% HNO_3, rinsed with demi- water. Wafers were dipped into 0.3 % HF for 5min., respectively, and rinsed in the demi- water to form -OH groups on the surface of SiO_2. These hydroxyl groups serve as reactive sites to initiate the film growth. When the wafer was loaded into the reactor, a Si- nucleation layer was grown by decomposition of Si_2H_6.

W- films were deposited with a sequence of Si_2H_6/WF_6 pulses, N_2 was used as a purging gas. A sequence of WF_6/ NH_3/ C_2H_4 /SiH_4/ NH_3 was applied to deposit W_xN_{1-x} films. Experiments were carried out

at 1 mbar. Variable parameters were temperature, pulse time, number of cycles. The temperature range was 250- 350 ºC. N_2 purging time was 2sec. The cycle time was 7.5- 11 sec for W and 14- 22 sec for W_xN growth. The amount of reactive gas was controlled by mass- flow controller for WF_6, Si_2H_6, NH_3, SiH_4 and C_2H_4 at 5 sccm with a total flow in the reactor of 45-80 sccm.

The composition of the films grown was measured with XPS (X- Ray Photoelectron Spectroscopy) using standard sensitivity factors. Surface roughness was measured with AFM (Atomic Force Microscopy). The thickness was calculated from the increase of the weight using the standard density for W of 19.3 and for W_2N of 17.2 g/cm^3.

C. Details of the resistivity test

A 4- point probe sheet resistivity test was performed in vacuum at a base pressure of $4*10^{-6}$ mbar at elevated temperatures. The measurements are done with a ramping up and down step of 0.01degree/ sec. The test includes the heating up step to 500 ºC for 30 minutes step at constant temperature and cooling down to room temperature. Stacks of Cu(100nm)/ Barrier/ SiO_2 and Cu(200nm)/ Barrier/ SiO_2 grown on Si- substrate are used for the test. Cu was deposited on wafers by rf-sputtering.

III. Results and Discussions

A. W growth in the Si_2H_6/ WF_6 system

W deposition was studied at the temperature range 250- 350 ºC. No temperature window for the deposition of W in ALD mode was found. Results of the experiments are shown in figure 1.

The growth of W films was about 3 to 5.7 monolayers/ cycle. Obviously, Si_2H_6 decomposes on the fresh W- surface, which is a well- known catalyst, with the formation of more than 1 monolayer of Si/cycle. All Si formed is consumed by the following WF_6 pulse. The adsorption of Si_2H_6 and high reactivity of WF_6 with Si are determining factors of a high growth rate.

The role of the Si- layer in the growth process was investigated at 325 ºC. The thinner the nucleation layer is, the slower the growth is on initial stages and the incubation time is longer, see figure 2. When the surface is converted into W, the growth rate for processes with a varying nucleation step is almost the same. The growth rate calculated from the slope of the growth curves is 4.5 monolayer/cycle for the Si_2H_6/ WF_6 ratio equal to 4/3 and 2/1.5. The growth rate is 3.6 monolayer/ cycle for the Si_2H_6/ WF_6 ratio equal to 1.4/2. This means that the nucleation layer helps to decrease the incubation time, but will not influence the final growth rate. The smaller incubation time of the growth the smoother the growing film is. AFM test showed roughness as high as 2.7 nm for 10 nm layer without nucleation and 0.52 nm for the nucleation at $2.3*10^7$ L.

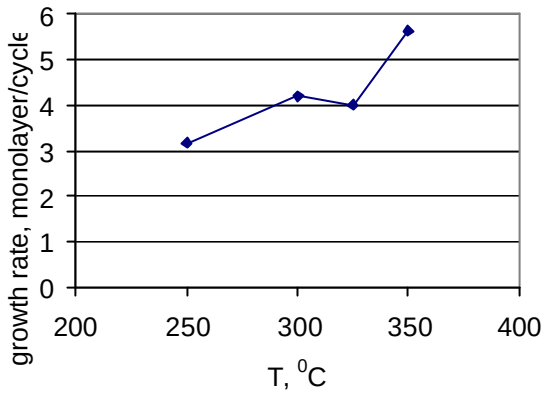

Figure 1. Temperature dependance of the W<Si> growth with a ratio of Si_2H_6 / WF_6 = 4/3 after 20 cycles, Si-nucleation layer was grown at exposure to $4.5*10^9$ L (Langmuir, 1L= 10^{-6} Torr*sec) of Si_2H_6. Growth rate was calculated from the total weight increase.

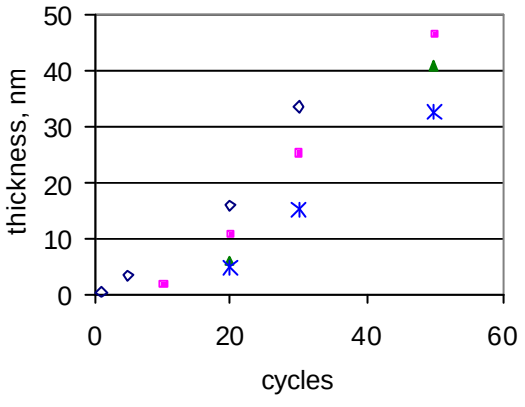

Figure 2. Thickness of W versus number of cycles at 325 C. In the legend:
○ is for Si_2H_6/WF_6= 4/3, nucleation at $4.5*10^9$L of Si_2H_6;
■ is for Si_2H_6 / WF_6= 4/3 and nucleation at $2.3*10^7$ L;
▲ is for Si_2H_6 / WF_6= 2/1.5 and nucleation at $2.7*10^5$ L;
✶ is for Si_2H_6 / WF_6= 1.4/2 and nucleation at $2.7*10^5$ L.

The resistivity of the grown films was in the range 160- 200 μΩcm for 25 nm films. The resistivity does not differ much with varying WF_6/ Si_2H_6 ratios, however the uniformity of the films does change. The best results based on STDV of resistivity were obtained for the WF_6/ Si_2H_6 ratio equal to 3/ 4 with a STDV of about 2 %, see figure 3.

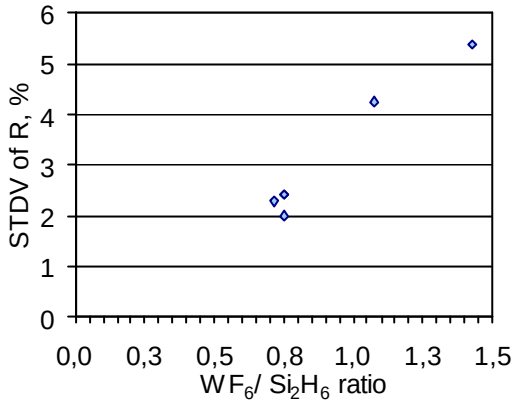

Figure 3. STDV of sheet resistance versus the ratio of WF_6 to Si_2H_6 for films with a thickness about 15 nm. The nucleation step is 4.5*10^9 L.

The deposited layers contain about 12 at% of Si according to XPS.

B. Growth of W_xN films in the WF_6/ NH_3/ C_2H_4/ SiH_4 system

$W_{1-x}N_x$ is reported to have a high resistivity of about 4500 μΩcm [3]. $W_xC_yN_{1-x-y}$ layers possess a resistivity of 300- 400 μΩcm with STDV of 3.5 % for 25nm films[2]. The C_2H_4 was chosen as a cheap carbon precursor and as an alternative to triethylborane (TEB). No continuous films were deposited with pulse sequences of WF_6/ NH_3/ C_2H_4, WF_6/ C_2H_4/NH_3. An extra step with a SiH_4 pulse (a sequence of WF_6/ NH_3/ C_2H_4/ SiH_4) resulted in roughness of 1.7 nm for a 20 nm film, due to direct interaction of Si with WF_6. That is not acceptable for a barrier application. A pulse sequence of WF_6/ NH_3/ C_2H_4/ SiH_4/ NH_3 was applied for the growth of $W_{1-x}N_x$ layers to prevent a direct interaction of Si with tungsten fluoride. No carbon and Si are incorporated however in the growing films. C_2H_4 and SiH_4 play a sacrificial role and all products formed with carbon and Si are removed. The effect of the C_2H_4 exposure on the films growth is not clear yet, Table 1, N 5-6.

Table 1. Summary table of the final growth rate and incubation time at different conditions

N	WF_6/NH_3/ C_2H_4/SiH_4/NH_3	T, ^{0}C	incubation time , cycles	growth rate, monolayer/ cycle
1	1/ 2/ 1/ 2/ 2	325	0,7	0,47
2	2/ 2/ 1/ 2/ 2	325	5,3	0,55
3	1/ 2/ 1/ 2/ 2 *4,5e9 L	325	no	0,47
4	1/ 2/ 3/ 2/ 2 *4,5e9 L	350	no	0,57
5	1/ 2/ 3/ 2/ 2	350	no	0,51
6	1/ 2/ 1/ 2/ 2	350	no	0,50
7	3/ 2/ 3/ 2/ 2	350	3,9	0,68

*). Process after a nucleation step with a large exposure to Si_2H_6 equal to 4.5e9 L

The temperature window for the $W_{1-x}N_x$ growth was limited to 325- 350 ^{o}C. It is not possible to go to lower temperature because of the formation of a WF_x·NH_3 adduct [4]. On the other hand, 350 ^{o}C is the maximum possible temperature in the back-end for Cu/SiLK combination. The growth rate was about 0.5- 0.6 monolayer/ cycle for a varying pulse time of C_2H_4 and WF_6, figure 4. The growth rate was calculated from the slope of thickness- cycles dependence, see figure 5.

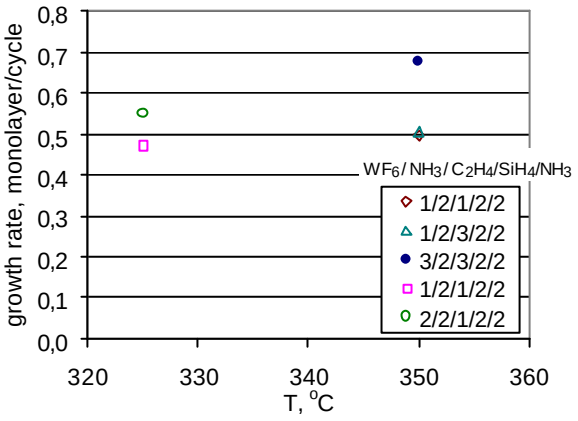

Figure 4. Growth rate of $W_{1-x}N_x$ versus temperature with varying pulse sequence of WF_6/ NH_3/ C_2H_4/ SiH_4/ NH_3. Time of reactive pulses is in the legend.

The thickness of initial Si film was the same for both temperatures (1.2 nm for 325 ^{o}C and 1.5nm for 350 ^{o}C) to equalize the starting conditions. Some experiments were performed after large initial exposure to Si_2H_6 4.5*10^9 L, figure 5. The thickness of the nucleation

layer influences how fast the growing film becomes continuous, but not the final growth rate. Incubation time of the growth, calculated from the growth rate, see Table 1, was very short or, in some cases, the growth started almost immediately. The short incubation time resulted in a roughness as low as 0.43- 0.76 nm for 16 nm $W_{1-x}N_x$ films. The films possess extremely low resistivity up to 340 μΩcm (STDV 2- 5%) for 10 nm films, compared to reported values [3].

The deposited films are $W_{1-x}N_x$ compounds with x= 15- 22at%. Nitrogen suffers from the preferential sputtering during XPS profile measurements [5], therefore the initial part of the obtained profile is more useful to estimate a real nitrogen concentration. No Si peak was measured at the Barrier/ SiO_2 interface.

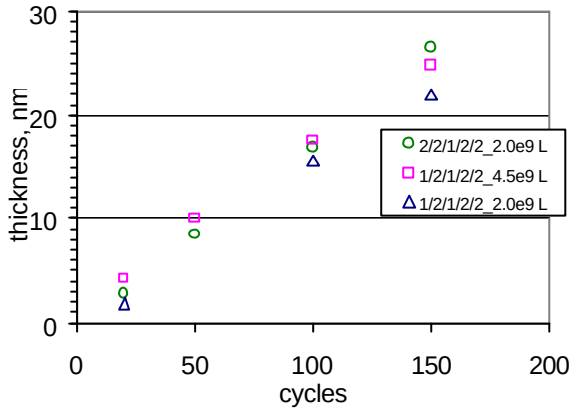

Figure 5. Thickness of the $W_{1-x}N_x$ films versus cycles at 325 ºC. Ratio of gas reactants with a sequence of WF_6/ NH_3/ C_2H_4/ SiH_4/ NH_3 is in the legend.

between Cu and Barriers occurred and the Cu/Barrier combination survived the 500 °C annealing test.

Table 2. Samples for the 4- point probe resistivity test with 100 nm Cu layer

N	barrier thick, nm	composition by XPS	Rbefore, mΩ/sq	Rafter, mΩ/sq	Rafter/ Rbefore
1		Cu/SiO_2	253	206	0,81
2	25,8	$W_{83}N_{17}$	450	225	0,50
3	20,5	$W_{83,5}N_{16,5}$	335	214	0,64
4	17	$W_{78}N_{22}$	365	235	0,64
5	26,3	$W_{84,5}N_{15,5}$	372	220	0,59
6	14,5	$W_{83.1}Si_{11.2}O_{5.8}$	310	206	0,66

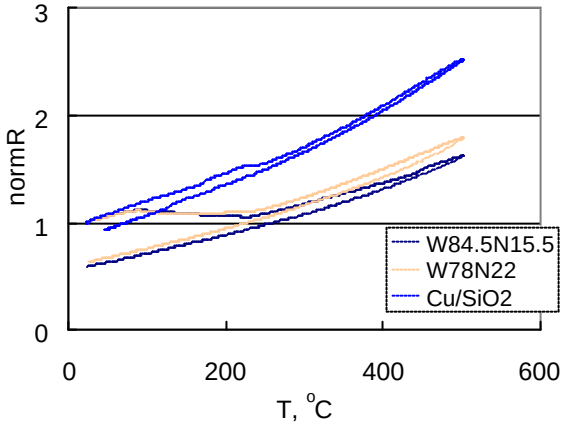

Figure 6. Normalized resistance change versus temperature during the measurements.

C. Resistivity test

Stacks of Barriers on SiO_2/ Si with 200 nm Cu layer show no change in normalized resistance after heating up to 500 ºC and cooling down to room temperature. Resistivity of Cu was 2.1 μΩcm. In contrary, samples with as deposited 100 nm copper film on SiO_2 are characterized by a resistivity of 2.53 μΩcm. Such an increase of specific resistivity is caused by the amount of defects in the Cu layer. The resistance of each sample is decreased after the test, Table 2 and figure 6. This lowering of resistivity corresponds to annealing of the defects in the thin Cu- layer. The resistivity approached 2.1 μΩcm and the TCR became 0.0028 deg^{-1} for each sample up to 100 ºC. Thus no reaction

IV. Conclusions

No ALD conditions for W growth are found in the WF_6/ Si_2H_6 system. Deposition rate is about 3-5 monolayers/ cycle at 250- 350 ºC.

The Content of Si in these W films was about 11-12at%. Resistivity was up to 200 μΩcm with STDV about 2% for 25 nm film

The growth rate in the WF_6/ NH_3/ C_2H_4/ SiH_4 system was about 0.5- 0.6 monolayer/cycle.

Grown films are $W_{1-x}N_x$ with x= 15- 22at % Resistivity of the deposited films was about 340 μΩcm with STDV of resistivity 2- 5 % for 10 nm films.

200 nm Cu metallization does not show any changes in resistance after the 500 ºC test. Annealed 100 nm Cu layer has the same specific resistivity as 200nm 2.1

μΩcm. No interaction of Barrier with Cu occurred during the annealing test up to 500 °C.

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