TiN Characterization Kye Okabe and Max Shulaker 6/6/2014

The first question we would like to address is the following: Why bother developing/ optimizing an ALD TiN recipe? There are several reasons for this. First, TiN is known to be a very good diffusion barrier, meaning that metals can be prevented from diffusing into a Si substrate by depositing a thin TiN layer and is widely used by the industry. Second, TiN has been proven to be functional as an electrode for Resistive Random Access Memory (RRAM). TiN is also relatively easy to etch (CMOS compatible), and is at the same time hard and dense. Although it is technically categorized as a ceramic, it has a relatively low bulk resistivity (20~30 μ Ω cm). Finally, it is also a biocompatible material, (FDA approved) and medical doctors often coat objects with TiN and implant them into patients!

As a different prospective, according to Mary Tang's "State of the Lab" talk in May 2014, the most enabled tool during the year of 2013 was the Fiji2, which along with Fiji1 are the only two tools in the SNF that are capable of producing Plasma ALD TiN as of June 2014. It is evident from the author's experience (K.O.) that well over 50% of recent usage on the Fiji2 is either for AlOx, HfOx, or TiN. More specifically, limiting the subject to TiN, members from P. Wong, S. Wong, Dionne, and Nishi's group have been regularly depositing TiN in the last month (May 2014). In addition to the academic teams, the author (K.O.) has also been recently contacted by members from Bosch and AcornTech to discuss about the discoveries that were made in this project. Despite the fact that TiN is highly in demand, there are no clear standards that show electrical or compositional parameters. Our goal is to establish the standards as of today, and moreover, suggest a better recipe for improved film qualities.

The next question we would like to address is what exactly is wrong or unsatisfactory with the current status. Fig. 2 summarizes the default or recommended Plasma TiN recipe as of today. The main parameters of the recipe calls for all heaters to be at 250 °C, a pre bake of an hour, process gas flow rates with 60, 200, 50 sccm of Ar (carrier), Ar (plasma), and N₂, respectively, and 300 Watts of plasma for a 20 sec duration per cycle. We grew 72~100 nm of SiO₂ using Thermco on L - Prime substrates and deposited 400cycles of the standard recipe at 250°C. With Prometrix, we measured a sheet resistance of $824\Omega/\Box$ at the center and $707\Omega/\Box$ at the edges

of the wafer, which under the assumption of 28nm film thickness is equivalent to $2307 \mu \Omega$ cm or $1980 \mu \Omega$ cm, which is roughly 2 orders of magnitude above the bulk resistivity of pure TiN (10~30 μ Ω cm). To get further insight of the bulk film properties, we decided to pursue an analytical method that would give us feedback of the atomic composition. Figure 7 summarizes the accessible analytical tools at SNC/SNL with its respective specifications. Our needs are a characterization method that is fast, μ m or larger lateral resolution to represent the true composition of the film, nm range depth resolution, and as accurate composition information as possible. For these reasons, the XPS PHI seemed to fit our needs the most and was utilized for composition characterization. We than took XPS measurements with Ar sputtering to get the atomic composition depth profile. The rise in oxygen levels to ~66% was the indicator of when we had penetrated through the TiN, and thus allowed us to extract just the TiN surface and bulk composition. For this report, we were consistent of using the following energy ranges for all XPS measurements.

C 279 ~ 292 eV N 392 ~ 402 eV O 526 ~ 536 eV Si 98 ~ 108 eV Ti 452 ~ 466 eV

A binary 25 smoothing was applied on our raw count signals to smoothen out rough curves and minimize noise. We confirmed that applying the smoothing once was sufficient for reducing noise levels and that C and O at% levels showed to be more consistent throughout the bulk. Fig. 1 shows the result of XPS measurements of a standard recipe shown in Fig. 2 at 250C. As the high resistivity indicated, we see that the TiN layer is contaminated with a significant amount of C (> 15%) and O (~10%).

The carbon contamination can be explained by insufficient reactions of the precursor, TDMA-Ti, which is loaded with CH₃ bonds. Oxygen, on the other hand, cannot be explained easily. Ideally speaking, we should not observe this because our recipe does not include a single material that contains O. It is therefore speculated that the source is either coming from poor vacuum or gasses/precursors that are being used. For further testing, we suggest that a gas check be performed at the feed point and exhaust of the Fiji. This way, we can determine whether the gasses and/or precursor is the source, or whether the chamber vacuum is the source. Another experiment that is slowly being done is to compare AJA TiN oxygen levels with Fiji TiN oxygen levels. In the AJA, the tool is equipped with a turbo molecular pump which allows to

create 10e-8 torr chamber conditions at pump down. Under the assumption that oxygen and water contents are negligible under these pressures, we should be able to obtain low O (few at% or less) TiN if the gasses are ultra pure. If funding is not an issue, we recommend to modify the Fiji in the following ways for low oxygen contamination.

- 1. Add oxygen and water filters to gas and precursor lines.
- 2. Connect a turbomolecular pump.
- 3. Add valves to the Ar line so they can be fully shut off.

The author would like to emphasize that adding a turbo molecular pump by itself is probably meaningless due to the fact that the Ar lines do not have valves to completely shut off the gas flow. Tests in Fiji 3, which is equipped with a turbo molecular pump indicates that even when setting all gas flows to 0 sccm, the chamber pressure cannot go below 1e-3 Torr.

With the given conditions and level of authority that the authors have, we therefore have no choice but to attempt to optimize the recipe and hope that we can minimize oxygen contamination rather than making modifications to the hardware which is what we think is the best solution.

We now return to Fig. 2 and consider what variables would be effective to tweak. As mentioned earlier, the carbon contamination indicates that the precursor has not fully reacted in the standard recipe. For this reason we decided to add more energy to the system by raising the chamber temperature as well as increase the plasma duration time. The temperature, however, is upper bounded by the decomposition of the precursor, meaning that there is a limit to how high we can raise the temperature before we get undesired artifacts. At temperatures too high the precursor breaks into smaller peaces and deposits on the surface.

Figure 6 shows the summary of plasma TiN films with relative parameters that were modified. Ptime indicates the plasma duration time, and pr/po indicates a pre heating of 1 hours in the chamber and 1 hour or more cooling in the LL under vacuum. The author (K.O.) also got qualified on XRD on Wed of the 10th week which was useful to measure the TiN film thickness and density shown in Sample y40. Note that all films were deposited for 400 cycles. Films that used the precursor labeled 92413, indicating that it was opened on September 24th of 2013, did not give a valid sheet resistance value due to the precursor being empty. Our record sheet resistance was

sub 80 Ω/\Box on sample 39 which is roughly an order of magnitude lower than sample 37, the standard recipe sample at 250 C . Despite the fair electrical measurements, the NH₃ films showed a lamella type of diffraction pattern on the surface with debris in some cases. There is likely margin for optimization, but the author stuck to N₂ films due to this observation. Figure 3 shows a trend that was observed from the sheet resistivity measurements. It appears that the sheet resistance has an exponential relationship with respect to plasma duration time, and saturates at around 3 minutes at ~90 Ω/\Box . Since we are concerned about the contamination in the bulk, we also measured the TiN bulk C and O at% levels for the various films as shown in Fig. 4 and 5, respectively. Fig. 4 shows the clear trend of decreasing carbon level with respect to increasing plasma time. More interestingly, Fig. 5 shows that the oxygen level does not decrease with increased plasma time. Rather it seems to be slightly increasing. From this we conclude that increased plasma time allows the CH₃ bonds to detach from the TDMA-Ti and leave the dangling N vulnerable to bonding with an alternate element. This alternate element, however, does not necessarily seem to always be Ti, but is also O as well. With increased plasma time, the CH₃ bonds decrease and Ti-N and Ti-O bonds increase, but the increase in Ti-N bonds appear to dominate the electrical properties and lower the resistivity.

With the given hardware configuration, we may have reached the lower limit of sheet resistance due to not being able to remove the oxygen bonds which are quite energetically favorable. However, in our final runs for the quarter (y43, y44, y46), we attempted to demonstrate a recipe that would have comparable resistance to the 3 or 5 min plasma/cycle recipe with much shorter time. The idea behind was that if we could deliver more excited state nitrogen to the surface of the sample, perhaps the plasma duration time could be reduced. The mean free path for the excited nitrogen state is known to be relatively low. For this reason, we increased the flow rate of plasma Ar which is used to assist maintain nitrogen's excited state to begin with. The tradeoff here is that we do not have independent control over the chamber pressure: It is simply determined by the flow rate of the gasses. When the plasma flow rate is increased, we have more excited species but on the other hand we have more collisions as well which gives opportunity for the nitrogen to lose its excess energy.

Nevertheless, y43 and y44 was performed with the parameters shown, but at 800 sccm plasma Ar instead of the default 200 sccm. The sheet resistance turned out to be quite competitive even with the 20 sec/cycle recipe (~100 Ω/\Box), but with a circular dark pattern across the wafer which was confirmed by XPS to be a form of TiNO_xC_y. It is thought that the increased pressure and Ar plasma facilitated reactions

of excited nitrogen for the most part of the surface, but within the plasma tube, some reactions occur in the gas phase and deposit circularly onto the wafer. In attempt to reduce this effect, sample y46 was run with 500 sccm instead which showed no obvious debris regions on the sample with somewhat higher sheet resistance.

In summary, we established a standard for sheet resistance for the standard recipe, established a standard for contamination levels via XPS, demonstrated improved recipes with up to an order of magnitude lower resistivity, established sheet resistance and contamination levels for several films, measured the thickness and density of one sample with XRD which can be used to assume film thickness needed for resistivity, and finally have demonstrated a proof of concept for minimizing the process time that is required for the high quality film recipes that we showed.



Figure 1. XPS Compositional Depth Analysis Std Recipe @ 250C

	Instruction	#	Value	Units
0	heaters	12-15	250	C
1	wait		3600	sec
2	flow	0(Ar)/1(Ar)/	60/200/50	sccm
3	pulse	1	0.06	sec
4	wait		5	sec
5	plasma		300	Watts
6	wait		20	sec
7	plasma		0	Watts
8	wait		5	sec
9	goto	3	400	cycles
10	end			

Figure 2. Plasma TiN Std Recipe before Modification



Figure 3. Exponential Dependence of plasma time vs sheet resistance at 270C



Figure 4. Carbon Contamination in TiN of various films measured with XPS PHI



Figure 5. Oxygen Contamination in TiN of various films measured with XPS PHI

ID#	Fiji#	temp	ptime	gas	RCA	pr/po	(Ω/□) flat	(Ω/□) center	(Ω/□) opp flat	5ptstd	nm	g/cm ³	date	precursor
y46	2	270	0.33	N2	У	у/у	-	139	180	21.22 19.318%			6/6	
y44/2	2	270	0.33	N2	У	у/у	100.9	84.54	131.7	21.22 19.318%			6/1	
y43/2	1	270	2	N2	У	y/y	80.74	92.22	92.39	5.746 6.349%			6/1	
y42/2	2	270	5	N2	У	y/y	82.53	84.55	-	3.829 4.373%			5/31	121213
y40/2	1	270	5	N2	У	y/y	-	83	102.4	10.06 10.932%	28.2	4.70	5/30	40114
y39/2	1	270	5	N2	У	у/у	78.57	80.29	98.69				5/30	40114
y37	2	250	0.33	N2	n	n/n	-	823.9	707.2	113.6 13.320%			5/30	121213
y36	2	300	2	N2	n	у/у	-	-	-	-			5/24	92413
y35	1	270	0.33	NH ₃	n	y/y	-	595.4	-	104 17.710%			5/24	40114
y34/2	1	270	1	NH3	n	у/у	-	372	225.8				5/23	40114
y33/2	1	270	1	NH ₃	У	у/у	278.7	244.7	274.3				5/23	40114
y32/2	2	260	3	N2	n	y/y	-	200k	-	5471. K 160.569%			5/23	92413
y31.5	2	260	3	N2	У	у/у	-	-	-				5/23	92413
y31	2	270	0.33	N2	n	y/y	518.5	529.9	673.6				5/18	40114
y30/1	2	270	1	N2	n	у/у	222.7	223.0	266.6				5/18	40114
y29/1	1	270	1	N2	n	y/y	180.7	200.6	269.1				5/18	40814
y28/1	2	270	3	N2	n	y/y	92.28	92.82	111.1				5/17	40114
a-y27 /2	1	270	3	N2	n	y/y	169.9	169.87	179.7				5/17	40114
y26/1	2	260	2	N2	n	y/y	115.3	114.4	131.5				5/4	40114
y24/1	2	250	1	N2	n	y/y	246.8	231.5	257.0				5/4	40114

Figure 6. List of TiN samples fabricated with relative parameters

	Signal in	Signal out	Lateral resolution	Depth resolution	Volume analyzed (x nm * z nm)	Minimum detectability (%)	Accuracy (%)	Specimen prep. (difficult/easy)	Characteristic of analyzed species (eg. E _K -E _L)
EPMA-WDS	electron	Photon (x-ray)	1-10 µm	1 µm	1 μm * 1 μm - 10 μm * 1 μm	0.1%	0.1-1%	easy	E _K -EL
SEM-EDS	electron	Photon (x-ray)	0.5–1 μm	100 nm – 1 μm	D nm 500 nm * 100 nm 1% 1-5% easy		E _K -EL		
TEM-EDS	electron	Photon (x-ray)	1 nm	10-100nm	1 nm * 10 nm - 1 nm * 100 nm 0.1-1% 1% difficult		difficult	E _K -EL	
STEM-EELS	electron	electron	0.2 nm	10 – 100 nm	00 nm 0.2 nm * 10 nm 1-5% 1%		1%	difficult	E _o -E _i
SAM	electron	electron	10 nm	1 – 5 nm	10 nm * 1 nm – 10 nm * 5 nm	1%	1-10%	easy	E _K -E _L - E _L
XPS	photon (x-ray)	electron	10 µm	0.5 – 5 nm	10 μm * 0.5 nm – 10 μm * 5 nm	1%	1%	easy	hv-E _i
SIMS	ion	ion	Nano-SIMS 50 nm	5 nm	50 nm * 5 nm	100 ppb	w/o standards ± 1000%, with standards ±1-10%	easy	m / q

Figure 7. Analytical tools accessible at SNC/SNL