

# Low Temperature Deposition of TiN by Plasma-Assisted Atomic Layer Deposition for System-in-Package Applications

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**Abstract** – A plasma-assisted atomic layer deposition (PA-ALD) process of titanium nitride (TiN) using  $\text{TiCl}_4$  precursor dosing and  $\text{H}_2/\text{N}_2$  plasma exposure is presented. *In situ* spectroscopic ellipsometry revealed a growth rate of  $\sim 0.7$  Å/cycle at 400 °C independent of precursor dosing. Varying the plasma exposure time changed the stoichiometry  $[\text{N}]/[\text{Ti}]$  of the films between  $\sim 0.93$ - $1.15$ . At 100 °C a relatively low chlorine impurity level ( $\sim 2$  at. %) and low resistivity ( $\sim 200$   $\mu\Omega\text{-cm}$ ) were obtained for a  $\sim 45$  nm thick film. The growth rate was found to be considerably lower ( $\sim 0.3$  Å/cycle) at this temperature. Using TEM imaging we found that PA-ALD TiN films can be deposited conformally in 20:1 aspect-ratio features (1.5  $\mu\text{m}$  width) but that the step coverage still needs to be improved.

**Index Terms** - Atomic Layer Deposition, Titanium Nitride

## I. INTRODUCTION

Titanium nitride (TiN) films can be found in a broad range of applications, for instance as diffusion barrier and metallization layer in back-end interconnect technology. For this application a low resistivity ( $< 500$   $\mu\Omega\text{-cm}$ ) film deposited conformally (step coverage  $> 90\%$ ) in these high aspect ratio structures ( $\text{AR} > 5$ ) is desired. Moreover, back-end and passive integration require process temperatures to be preferentially  $< 350$ - $400$  °C. The atomic layer deposition (ALD) technique shows great potential in meeting these requirements. Good TiN film properties in terms of resistivity ( $< 200$   $\mu\Omega\text{-cm}$ ) and step coverage (75%, AR up to 85) were obtained using ALD with titanium tetrachloride ( $\text{TiCl}_4$ ) and ammonia ( $\text{NH}_3$ ) precursors at a deposition temperature of 400 °C [1]. At lower temperatures, however, the chlorine (Cl) impurity level in the

film was observed to increase rapidly. Ammonium chloride ( $\text{NH}_4\text{Cl}$ ), formed during the  $\text{NH}_3$  pulse, which sticks to the surface at temperatures below 370 °C was mentioned as a possible explanation for the increased Cl level. This shows that  $\text{NH}_3$  is a less suitable reducing agent for deposition in this temperature range. Also the resistivity tends to be higher at low deposition temperatures and this is possibly related to the relatively high level of Cl impurities.

In this contribution, we investigate the use of nitrogen and hydrogen radicals produced by an inductively coupled  $\text{H}_2\text{-N}_2$  plasma to replace  $\text{NH}_3$  as reducing agent in the TiN ALD process. The abstraction of Cl from the adsorbed  $\text{TiCl}_x$  precursor by plasma-produced H radicals is reported to be almost independent of the deposition temperature [2]. N radicals from the plasma lead to nitridation of the growing film, forming TiN. This should enable us to deposit TiN films at low deposition temperature while maintaining a low resistivity and low impurity content. This so-called plasma-assisted atomic layer deposition (PA-ALD) process, also referred to as plasma-enhanced-ALD, has already shown potential in the deposition of Ti, Ta, and TaN metallic films [3,4]. We hereby extend the current research on (PA-)ALD of metals and their nitrides as recently reviewed by Kim [5] with the PA-ALD process of TiN while also going down in deposition temperature to 100 °C.

Besides the interest for the metallization of dual damascene features in back-end processing of ICs, we investigate the possibility of using PA-ALD in the relatively new field of 3D integration of stacked die configurations in so-called System-in-Package (SiP) devices. In these devices specific functions such as embedded wireless networks, DRAM, embedded processors, etc. will be combined into one product. The stacked wafer dies will be connected by through-wafer vias with aspect ratios up to 50. Here, we specifically studied PA-ALD TiN film conformality and uniformity in macropores (20:1 AR). These are present in MOS high-density capacitors that can be integrated in these SiP devices for rf decoupling purposes.

## II. EXPERIMENTAL

The depositions were carried out in a home-built PA-ALD reactor as shown schematically in Fig. 1 and which is similar to the one described by Rosnagel *et al.* [3]. The substrates are loaded onto a resistively heated substrate holder (2 inch, 100-400 °C) within a wall-heated low-pressure deposition chamber (20-200 °C,  $10^{-6}$  Torr base pressure).

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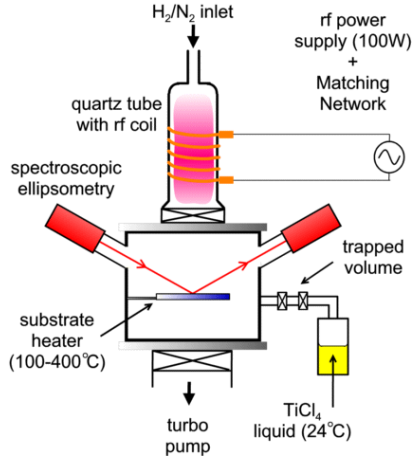


Fig. 1. Schematic drawing of the plasma assisted ALD (PA-ALD) reactor.

The operation of the PA-ALD setup will be explained on the basis of the TiN deposition cycle as shown in Fig. 2. During step 1, the  $\text{TiCl}_4$  precursor dosing, the deposition chamber is separated from the pumps and the plasma source by gate valves. The  $\text{TiCl}_4$  precursor is dosed using a so-called trapped volume directly connected to the  $\text{TiCl}_4$  source that is kept at room temperature. From this trapped volume a controlled amount of  $\text{TiCl}_4$  vapor is fed into the reactor resulting in an operating pressure of typically  $\sim 3 \cdot 10^{-3}$  Torr. After typically 5 s of dosing the excess amount of  $\text{TiCl}_4$  is diluted by argon and purged out of the reactor by opening the valve to the pumps. During step 2, the gate valve to the inductively coupled plasma source (100W,  $10^{-2}$  Torr operating pressure) is opened. The radiofrequency plasma source, consisting of a multiple-turn copper coil wrapped around a quartz tube, is operated using a mixture of  $\text{H}_2$  and  $\text{N}_2$  gases. After switching off the plasma, the vessel is pumped down to base pressure in preparation of the next cycle. The reactor is equipped with optical access ports for *in situ* studies of TiN film growth by spectroscopic ellipsometry (SE) over the photon energy region of 0.7-5.0 eV.

### III. TiN MATERIAL PROPERTIES

(PA-)ALD is based on the principle of self-limiting surface reactions during the sequential precursor exposure steps that limit the growth rate to a maximum of one monolayer of film growth per cycle. To investigate this for our TiN PA-ALD process we used *in situ* spectroscopic ellipsometry (SE) [6]. TiN films were deposited on n-type c-Si wafers with a  $\sim 2$  nm native oxide. The thickness was monitored with SE by taking a measurement after every 10 completed cycles. The growth rate was determined from the slope of thickness versus number of cycles.

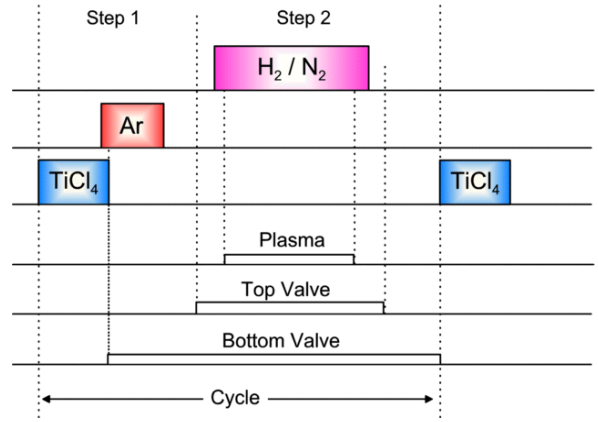


Fig. 2. TiN deposition cycle based on  $\text{TiCl}_4$  dosing (step 1) and  $\text{H}_2$ - $\text{N}_2$  plasma exposure (step 2).

This was done as a function of the precursor dosing and the plasma exposure time at a deposition temperature of  $400^\circ\text{C}$  as shown in Fig. 3. The growth rate proved nearly independent of the  $\text{TiCl}_4$  precursor dosing indicating that the surface is basically saturated by adsorbed  $\text{TiCl}_x$  precursor groups during these exposure times. With increasing plasma exposure time  $t_{exp}$  the growth rate starts to level off at  $\sim 0.7 \text{ \AA}/\text{cycle}$  at  $t_{exp} = 15$  s but still increases slightly when going to exposure times  $> 60$  s. Under these conditions it is expected that almost complete abstraction of Cl by the plasma-produced H radicals occurs. Another effect of the plasma exposure time is the change in stoichiometry ( $[\text{N}]/[\text{Ti}]$  ratio), ranging from 0.93 at  $t_{exp} = 5$  s to 1.15 at  $t_{exp} = 60$  s as determined with Rutherford Backscattering (RBS). The optimal settings resulting in stoichiometric ( $[\text{N}]/[\text{Ti}]=1$ ) films were found to be 15 s of plasma exposure and 5 s of precursor exposure time. Including the purge and pump steps, the total time per cycle was 60 s.

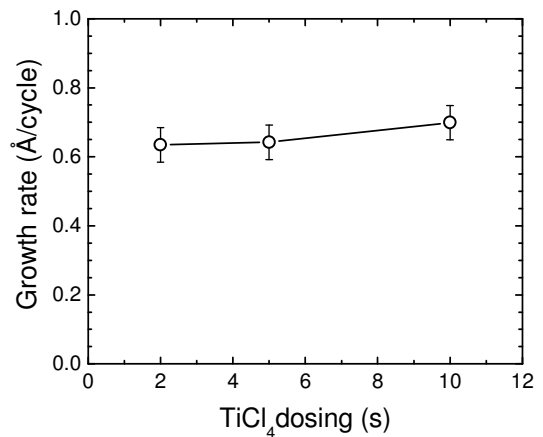


Fig. 3. The growth rate as a function of the  $\text{TiCl}_4$  dosing as determined with *in situ* spectroscopic ellipsometry (SE). The growth rate was determined during deposition by dividing the increase of thickness of the TiN film by the number of cycles. When varying the  $\text{TiCl}_4$  dosing, the plasma exposure time was kept constant at 15 s.

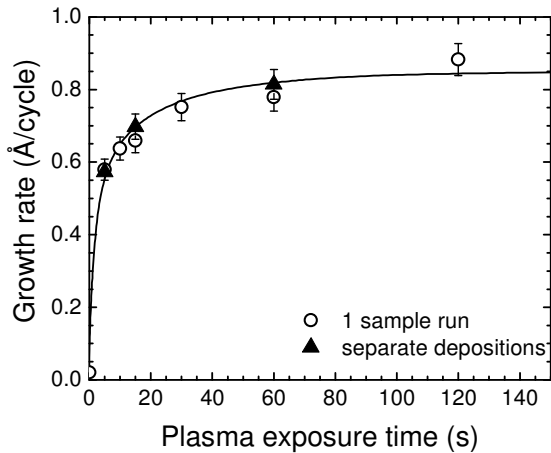


Fig. 4. The growth rate as a function of the plasma exposure time as determined with *in situ* spectroscopic ellipsometry (SE). The growth rate was determined during deposition by dividing the increase of thickness of the TiN film by the number of cycles. When varying the plasma exposure time, the  $\text{TiCl}_4$  dosing time was kept constant at 5 s. The values are confirmed by measurements of the growth rate in separate deposition runs.

Thin TiN films ( $\sim 10$  nm) were deposited at different deposition temperatures using the optimal settings. At low temperature the growth rate decreases but appears to stabilize at  $\sim 0.3$  Å/cycle (Fig. 5). Previous studies suggest that the abstraction of Cl by plasma produced H radicals is almost temperature independent [2], whereas the amount of adsorbed  $\text{TiCl}_4$  precursor on the surface is reported to increase with lower temperatures due to a higher surface residence time [7]. Our results might therefore imply that the growth process is limited by the number of reactive surface sites present after a cycle, i.e. the number of, for example,  $\text{NH}_x$  surface groups formed during the plasma exposure step. The SE data was analyzed using the Drude-Lorentz parameterization of the dielectric function and the resistivity of the film was *in situ* determined from the Drude term in the near-infrared region (Fig. 5). The increase in resistivity at low deposition temperature is expected to be related to the increased amount of Cl-impurities in the film. Using RBS the Cl-impurity level in these  $\sim 10$  nm films is found to increase from  $\sim 0.2$  at. % at  $400$  °C to 7 at. % at  $100$  °C.

For thicker films ( $>40$  nm) deposited at  $100$  °C, however, lower resistivities ( $\sim 200$   $\mu\Omega\text{-cm}$ ) and lower Cl impurity levels ( $\sim 2$  at. %) were found. These values are relatively low for an ALD process at these low temperatures. RBS measurements of these thicker films also revealed that the Cl is predominantly present on the film interfaces. Also *ex situ* four-point probe measurements of the resistivity were performed and for thick films the obtained resistivities were in agreement with the SE values. However, for the  $\sim 10$  nm films the four-point probe measurements yielded somewhat higher values most probably due to oxidation after exposing the films to air. *In situ* measurements by SE are therefore preferred over the *ex situ* measurement by the four-point probe.

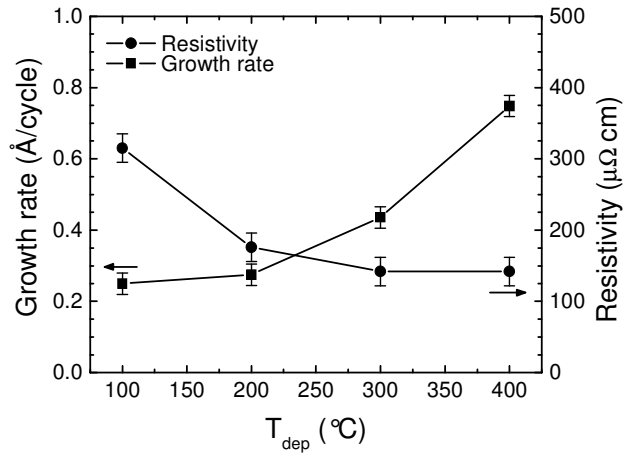


Fig. 5. The growth rate as a function of the deposition temperature as determined with *in situ* spectroscopic ellipsometry. From the near-infrared part of the dielectric function deduced from the ellipsometry data the resistivity of the film was determined before removal of the sample from the vacuum. This provides insight into the resistivity of the very thin films before oxidation when exposed to air.

#### IV. APPLICATION OF PA-ALD TiN FILMS

High-density MOS capacitors are fabricated on highly-doped Si-wafers with arrays of high-aspect ratio features with a diameter of  $\sim 1.5$   $\mu\text{m}$  referred to as “macropores” [8]. Using the Bosch process the macropores are dry-etched to a depth of  $\sim 30$   $\mu\text{m}$  or more and the surface is subsequently covered with an ONO (oxide/nitride/oxide) dielectric stack. The top electrode usually consists of n-doped poly-Si and requires a furnace anneal of  $1000$  °C step to improve conductivity. In the future, the capacitance per area can be improved by using a high-k dielectric and enlarging the surface area by increasing the macropore aspect-ratio and decreasing the pitch. Therefore, preferably a metallic film as top electrode deposited conformally at a low deposition temperature is desired. Here we deposited a TiN top electrode using our PA-ALD process at  $400$  °C and we studied the degree of conformality (step coverage) of the TiN film in the macropore.

Cross sectional TEM images of the device stack are shown in Fig. 6. The  $\sim 40$  nm thick TiN film was covered by a  $\sim 0.7$   $\mu\text{m}$  thick poly-Si layer deposited by LP-CVD at  $750$  °C for imaging purposes. The TEM imaging revealed that the TiN film was deposited conformally on top of the ONO stack along the surface of the macropore and that the TiN appears to be somewhat polycrystalline.

The image in Fig. 6a was made with a high angle annular dark field (HAADF) detector in the TEM using the elastically scattered electrons for imaging. The HAADF detector is therefore mass sensitive, which means that higher brightness in the image corresponds to the presence of (a larger concentration of) heavier atoms. Upon closer inspection we observed that the thickness of the film varies along the sidewalls of the macropore. A minimum film thickness of  $\sim 7$  nm was found on the sidewall at  $\sim 5$   $\mu\text{m}$  above the bottom of

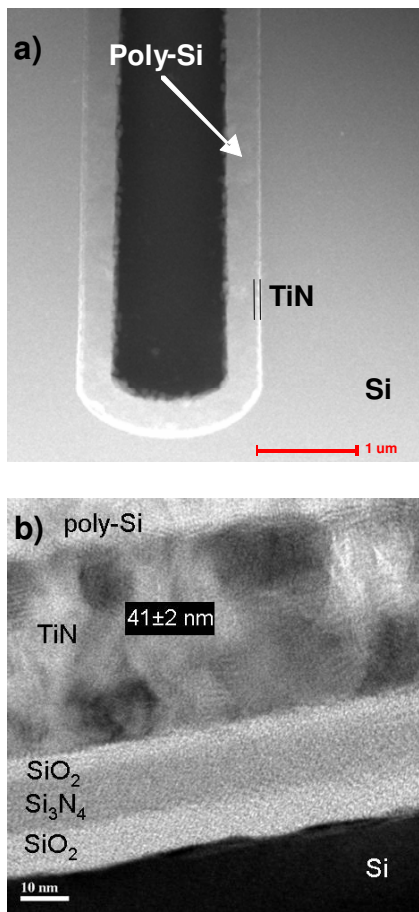


Fig. 6. TEM images of a “macropore” with a ONO dielectric stack covered with a PA-ALD TiN film and capped by Poly-Si. a) Low magnification view of the bottom part of the macropore visualized by use of a high angle annular dark field detector. b) TiN deposition profile at the top part of a macropore. The TiN film acts as a top electrode in the high density MOS capacitor layer stack deposited onto the macropore structures.

the feature compared to a thickness of 28 nm measured at the bottom.

To explain this deposition profile, we suggest that not all the surface of the macropore is exposed to the same amount of radical flux during the plasma exposure limiting the growth process in some areas. Since the  $\text{TiCl}_4$  precursor is introduced at a very low pressure and has no loss processes other than sticking to the wall it is assumed to cover the complete surface of the macropore. We propose that surface loss processes limit the Knudsen transport of the plasma-produced radicals within the feature. Besides the abstraction of Cl by H radicals forming HCl and the nitridation of the material by N, also recombination processes of these plasma-produced radicals at non Cl-terminated sites should be taken into account. From simple geometric considerations including reflection of the radicals at the macropore walls one can find that the radical

flux decreases gradually along the sidewalls ending in a minimum close to the bottom of the macropore. Because surface loss of the H and N plasma radicals can be significant during their transport within the macropore (compared to blanket films) the Cl abstraction and nitridation step may not have reached saturation yet. This possibly explains the limited step coverage at a distance of  $\sim 5 \mu\text{m}$  from the bottom of the macropore. We expect that by prolonging the plasma exposure time the step coverage improves.

## V. CONCLUSIONS

The results on the PA-ALD process of TiN using  $\text{TiCl}_4$  precursor and a  $\text{H}_2\text{-N}_2$  plasma show that the process has the ALD characteristic of self-limiting surface reactions both during  $\text{TiCl}_4$  and plasma exposure. The potential of PA-ALD for depositing films with good material properties at low temperatures is shown by a relatively low resistivity ( $\sim 200 \mu\Omega\cdot\text{cm}$ ) and a low Cl impurity content of  $\sim 2 \text{ at. } \%$  obtained for a  $\sim 45 \text{ nm}$  thick film at  $100^\circ\text{C}$ . With PA-ALD a TiN film was deposited in macropore structures (20:1 AR) that are used in high-density MOS capacitors. We attribute the variation of film thickness along the macropore sidewalls to plasma radical recombination loss at the walls during the plasma exposure step. The effect of prolonged plasma exposure time will be explored in future work.

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