ECS Transactions, 13 (1) 459-464 (2008)
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Novel Batch Titanium Nitride CVD Process for Advanced Metal Electrodes

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This article describes a novel CVD process for Titanium Nitride (TiN) films developed in a 300 mm vertical furnace. We have solved Chlorine incorporation at low temperature inside the TiN layer while at the same time the batch process yields a 3 times higher throughput per dual reactor system compared to a single wafer system with 3 chambers. We show process results for load sizes ranging from 5 to as much as 100 wafers that prove filler wafers are only required to a minimum. Applications with the developed TiN process are in Metal-Insulator-Metal memory devices such as Stack DRAM, and embedded DRAM.

Introduction

Memory devices for the generations beyond 65 nm will be based on Metal Insulator Metal (MIM) capacitor cell structures. The most promising candidate for both metal electrodes (top and bottom) is Titanium Nitride (TiN) as shown for instance by the ITRS roadmap for Front End Processes [1]. A significant part of these electrodes are applied in the DRAM memory cell [2,3]. But also in gate stack development for advanced CMOS beyond 45 nm technology node TiN is widely used as mid-gap metal gate electrode [4]. The material is applied as control gate electrode in NAND Flash [5], as well as heater electrode and control gate electrodes in phase change memory [6]. Furthermore next generation MIM capacitors for embedded Memory devices target TiN as the electrode material. Historically metal nitrides were deposited by single wafer deposition tools. This article describes a novel CVD process for TiN films developed for the first time in a 300 mm vertical furnace at low pressure.

Chemical Vapor Deposition

TiN films can be grown by conventional CVD using $TiCl_4$ and NH_3. The resulting resistivity of the film is too high for the application as electrode material in semiconductor devices. Therefore we used a pulsed CVD process [Fig. 1].

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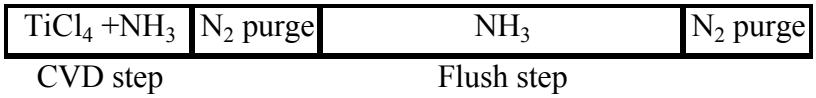

Figure 1. The novel batch CVD process for TiN. The first part of the cyclic process is a true CVD step; the second part is a selflimiting NH_3 flush step.

After a TiN CVD step that typically grows a thin film of 1 Å, the gases are purged out of the reactor and a NH_3 flush step is introduced resulting in a thin uniform film. The second step is a self-limiting step. The cycle is than repeated until the required film thickness has been reached. The process window is broad and has been investigated in the temperature range of 350 to 500°C. A lower temperature than 500 °C yields more Cl trapped in the growing film and thus a higher film resistivity. TiN films grown in conventional ALD-mode with $TiCl_4$ and NH_3 have a major disadvantage in the growth per cycle of only 0.2 Å [7].

Reactor

The process was developed in a dedicated reactor that is part of the A412 vertical furnace platform: A quad boat dual reactor vertical batch furnace for high volume manufacturing. This system is described in detail elsewhere [8]. Next to the use of a conventional heater and quartz walled tube that forms the reactor chamber inner wall a multi-hole injector system inside the reactor chamber has been introduced. $TiCl_4$ delivery was done by means of a commercially available direct liquid injection system capable of delivering up to 1.5 g/min of $TiCl_4$ pre-cursor. Such a system consists of a liquid flow controller, a vaporizer and a mass flow meter downstream of it. NH_3 gas of semiconductor grade is delivered by conventional mass flow control units. The pressure in the reactor is controlled in a range between 10 and 10000 mTorr with an accuracy of ± 1 mTorr. To prevent particle formation by peeling of the grown TiN film on the quartz, a thermally activated in situ cleaning process has been developed using NF_3 and Cl_2 gases to remove TiN effectively from the chamber walls. The lower part of the reactor chamber is sealed of by a vacuum door plate that is heated by resistive electrical heating to prevent condensation reaction byproducts. A high purity N_2 purged mini-environment controls the O_2 levels well below 10 ppm. This is very important to keep the resulting resistivity of the film in control. An experiment was performed to establish the influence of O_2 level in the mini-environment below the closed entrance of the reactor both during processing as well as during the so–called “boat-out” step of the process recipe in which the carrier with silicon wafers is lowered about 1300mm down from the reactor at a speed of 100mm/min. During this lowering the wafers start cooling down in the mini-environment from 300 °C to room temperature. In Table I the effect on resistivity has been given for a high O_2 concentration (>1000ppm) in the mini-environment and a well controlled mini-environment with O_2 levels at 12 ppm.

TABLE I. O_2 level experiment				
O_2 level during Deposition (@500 °C)	**O_2 level during "Boat-out" (@300 °C)**	**TiN Rs (Ω_{sq}) Bottom Wafer**	**TiN Rs (Ω_{sq}) Centre Wafer**	**TiN Rs (Ω_{sq}) Top Wafer**
>1000 ppm	>1000 ppm	610	721	945
>1000 ppm	13 ppm	315	378	403
12 pmm	12 ppm	284	291	297

Clearly the effect on sheet resistance is present when O_2 level is high. The wafer that is introduced into the mini-environment last with relative highest temperature (i.e. the top wafer in the carrier) has highest R_s value.

Productivity

The flexibility in load size is illustrated in Figure 2 where the deposited thicknesses for 3 different Product wafer load size processes with one and the same recipe are given.

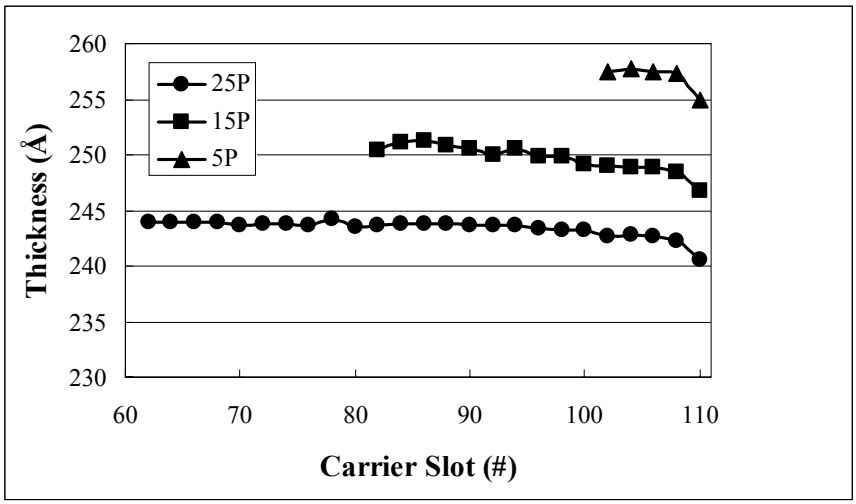

Figure 2. Flexible load size performance of the pulsed CVD TiN process for 5, 10 and 25 Product wafers in the furnace.

Per Product wafer a constant decrease of 0.7 Å in thickness is measured. For the 3 different load sizes only 3 filler wafers were used. Slot 6o corresponds to the centre of the reactor. Slot 110 is the top of the furnace. For films with a thickness of 10 nm the dual reactor system produces as much as 75 wafers per hour. This is about 3 times higher a throughput per dual reactor system than the combined throughput of a single wafer system with 3 chambers.

Composition

Stochiometric TiN films are generated with thickness uniformities of 1% range using the pulsed CVD process at 500 °C deposition temperature. The results of Auger analysis on film composition are given in Table 2. The Chlorine contamination is well below 1 at.%. Depth XPS measurements confirmed the low Cl content below 1%.

TABLE II. Composition analysis

Element	Wafer Top	Wafer Bottom	Reference
Ti(%)	48.7	49.0	47.5
N(%)	49.0	49.0	47.5
O(%)	1.6	1.3	2.0
Cl(%)	0.7	0.7	3.0
N:Ti	1.01	1.00	1.00

The last row contains the ratio between the Nitrogen and Titanium elements. The column on the right contains reference data of a single wafer deposition system.

The low concentration of Cl in the film is a result of the two step process where the self-limiting NH_3 flush following the CVD deposition step removes most of the Cl content from the freshly deposited TiN layer. As a result he thin film resistivity value of these films measure as low as 150 μΩcm. When the ratio of the NH_3 flush step time vs. the $TiCl_4$+NH_3 CVD step time is reduced from 2:1 to 1:1 the resistivity increases by a factor 2 due to the increased Chlorine content of the film.

Conformality

In memory structures the conformality of the electrodes are essential for proper electrical performance, minimizing the variation of resistivity. Conformality in this paper is defined as 100% minus the relative maximum full range of the thicknesses of the film measured in the top, center and bottom of the trench respectively. Step coverage is the ratio between the thickness of the film deposited on the sidewalls of the trench structures and the thickness of the film deposited on the surface of the wafer. Step coverage in the range of 85 to 95% is measured for an aspect ratio (AR) up to 40:1. Although the TiN film is grown in CVD-mode even films in deep trenches with high aspect ratio (AR=80:1) have been successfully deposited in a 100 wafer load batch with good step coverage and conformality within the trench higher than 80%. In Figure 3 the cross-section SEM image is shown for a pulsed-CVD 50nm TiN film grown at 500°C in an AR=32:1 trench. The conformality observed is >92%.

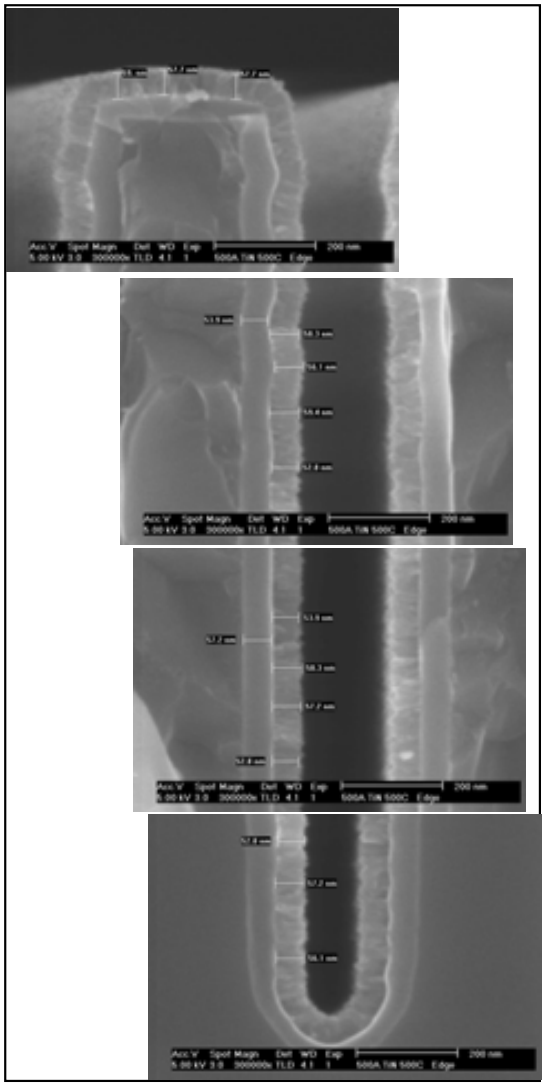

Figure 3. Cross-section SEM analysis of 50nm thick TiN deposited by pulsed-CVD in a trench with AR=32:1. A conformality >92% is measured.

Conclusions

We have developed a novel batch CVD process for low resistivity TiN films using a 300 mm vertical furnace. The reactor hardware has been specially designed to yield low particle performance and ease of maintenance for the TiN process. The pulsed CVD process results in highly conformal, stochiometric layers with low Chlorine (<1%) and low Oxygen (<1.7%) concentrations and uniform thickness distribution within the 300 mm silicon wafers processed in the reactor. A dedicated injection system enables high uniformity of deposited films on 100 product wafers distributed from bottom to top of the furnace and results in productivity of the dual reactor system of over 75 wafers per hour.

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