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Advanced characterizations of fluorine-free tungsten film and its application as low resistance liner for PCRAM

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A B S T R A C T

Using a metal-organic tungsten based precursor, a fluorine-free tungsten thin film has been obtained. The process deposition recipe includes a plasma-enhanced CVD (PECVD) step and atomic layer deposition (ALD) cycles. A set of physicochemical characterizations including X-ray reflectivity (XRR), in-plane X-ray diffraction (XRD), wavelength dispersive X-ray fluorescence (WDXRF), plasma profiling time of flight mass spectrometry (PPTOFMS) and microscope observations has been realized in order to study the W thin film structure and properties. The film is perfectly conformal whatever the structure size investigated (from tens of nanometers to micrometers wide). It was also highlighted that the F-free W film exhibits the lowest electrical resistivity phase (α-W) but is not pure. Indeed, in addition to a top surface oxidation, a layer located at the W film / substrate interface is present. This interface layer (IL) contains impurities, including carbon and oxygen, due to ligand decomposition. This IL might be deposited during the soak step or during the PECVD step.

The W liner with thicknesses ranging from 3 to 4 nm has been implemented on PCRAM structures in order to evaluate its impact on contact plug resistivity. First electrical results are promising and demonstrate the interest of using a F-free low resistance W liner. At the aspect ratio studied, the gain in terms of contact plug resistivity is about 20% compared to the process of reference using a TiN liner. Modeling shows that this benefit is mainly due to the reduction of interface resistances.

1. Introduction

Currently, interconnect technology is widely dominated by copper metallization. The conventional plug is made of TaN barrier / Ta liner / Cu seed layer (Physical Vapor Deposition, PVD) / Cu fill (Electrochemical Deposition, ECD). Nevertheless, as feature sizes decrease for advanced technologies, efficient copper metallization and interconnect reliability are becoming real challenges for future manufacturing. Since for line width below 30 nm a dramatic increase of the wire resistance is observed, many metallization schemes are currently under development [1–3].

Various options are investigated: (i) using Cu, new barrier and liner combinations are being investigated and (ii) Cu fill replacing by alternative metals is also studied. For instance, Co and Ru liners have been proposed in order to improve damascene Cu gap-fill [4,5] and the use of Mn-based barrier has been demonstrated to reduce line resistance [6]. Filling via with Co without any barrier promises resistance and/or yield benefit at around 15 nm via CD [7]. Ruthenium is also studied as an alternative metallization for future technology nodes with wire widths of 10 nm and below [8,9].

In parallel to Cu metallization, tungsten plug processes have been widely used in the most advanced semiconductor devices [10,11]. Due to his low resistivity and conformal bulk fill in high aspect ratio and narrow features, W metallization is a serious alternative to the Cu one. Cu suffers from different shortcomings. As described previously, the first one is the resistivity size effect, namely, the rise in electrical resistivity when sample structural dimensions (thicknesses in case of films, line heights and widths in case of interconnects) are reduced. This is linked to its relatively large electron mean free path (EMFP) of 39 nm at room temperature [12–15]. On the other hand, the upper limit to the EMFP of W has been reported as 10 nm [16]. Therefore, even if the room-temperature bulk resistivity of W at 5.3 $\mu\Omega$.cm is more than three times higher than for Cu at 1.7 $\mu\Omega$.cm, the resistivity of W is predicted to cross below that for Cu at linewidths below 25 nm [17]. In addition, the

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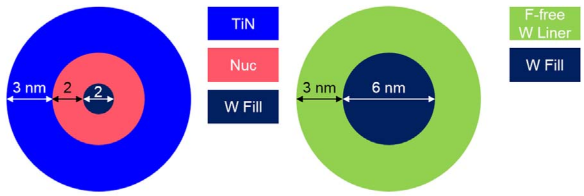

	Conventional process		F-free W liner	
	Thickness	*% Area Occupied*	*Thickness*	*% Area Occupied*
Barrier	3 nm	75 %	3 nm	75 %
Nucleation	2 nm	22.2 %	No nucleation layer	
W Fill	2 nm	2.8 %	6 nm	25 %

Fig. 1. Schematic representation of conventional tungsten plug process and the use of F-free W liner for a 12 nm contact hole.

second shortcoming is the degraded reliability of Cu as device operating temperatures and current densities increase with each technology node. Electromigration is the main factor to explain the reliability issues [18–20]. The higher melting temperature of tungsten (more than twice of copper) should result in improved interconnect reliability, qualitatively similar to the improvement observed when Cu was introduced to replace Al interconnects [21].

In tungsten plug process, the traditional metallization has used the sequential following scheme: TiN / SiH_4 or B_2H_6 nucleation layers / WF_6 CVD W, where the TiN (3–5 nm) acts as both an adhesion layer on dielectrics and a barrier to F dissemination during the CVD W process. The nucleation layer (2–3 nm) serves as a nucleation layer for the low resistance CVD W. This conventional process may no longer be extendable to high aspect-ratio small contact holes. Indeed, for a 10–15 nm contact hole all the volume will be occupied by the barrier and the nucleation layer. This phenomenon is evidenced for a 12 nm contact hole on Fig. 1. The major challenge for W fill scaling is thus to improve the line R_s and R_c by increasing the volume of the low resistance CVD W bulk material. So far, TiN has been the best known material to provide an adhesion layer for CVD W and to restrain fluorine diffusion but a nucleation layer is then required before CVD W. Fluorine-free tungsten film has been recently suggested as an ideal solution to substitute the high resistance TiN and B_2H_6 nucleation layer [22,23].

In this work, by using a metal-organic tungsten based precursor, a fluorine-free tungsten thin film has been obtained using plasma-enhanced CVD step and ALD cycles. The structure and properties of the tungsten thin film have been studied using a set of physicochemical characterizations. Finally, the low resistance W liner has been implemented on PCRAM structures in order to evaluate its impact on contact plug resistivity.

2. Experimental details

A Volta™ CVD W chamber has been installed on a 300 mm Applied Materials Endura platform. This chamber enables a fluorine-free tungsten deposition. Deposition temperature is set at 180 °C. The sequence used for this study consists in a first step of precursor soak, then a plasma-enhanced CVD (PECVD) step is performed and finally atomic layer deposition (ALD) cycles are realized. The soak and PECVD steps lead to a film thickness of about 1 nm (XRR measurement); the desired thickness is then modulated by the number of ALD cycles. Argon is used as carrier gas and a metal-organic tungsten compound provided by Entegris under the name Joppa27™ is used as tungsten precursor. Regarding the safety data sheet, this latter compound is doubtless based on tungsten carbonyl $W(CO)_6$. During the ALD process, Ar/H_2 plasma is used as a counter-reactant to reduce primary species into W film. In order to isolate the W films from the Si(100) substrate, all depositions have been realized on a 100 nm thick thermal silicon oxide (except for WDXRF analyses where W films were directly deposited on Si).

The sheet resistance of samples was measured by using a fully automatic 4 point probe sheet resistance Napson WS-3000 tool, X-ray reflectivity (XRR) spectra were acquired on a Jordan Valley JVX5200 X-ray reflectometer, in plane X-ray diffraction (XRD) was performed on Rigaku SmartLab high-resolution X-ray diffractometer, depth profiling was achieved using a Horiba Jobin Yvon Plasma Profiling Time Of Flight Mass Spectrometry (PPTOFMS) instrument and Wavelength Dispersive X-ray Fluorescence (WDXRF) was realized on Rigaku AZX400 sequential WDXRF spectrometer. Hitachi S-5500 scanning electron microscope (SEM) was used to observe conformality of tungsten films in contact plugs. For PCRAM structures, additional transmission electron microscopy (TEM) observations were performed and contact plug resistivity was evaluated using a 2-wire resistance test on a chain of contacts.

3. Results and discussion

3.1. Physicochemical characterization of tungsten films

The resistivity of F-free W (solid circles) films as a function of thickness in the as-deposited state has been plotted on Fig. 2. For comparison, values obtained for TiN film (open circles) traditionally used as adhesion layer and F barrier have been added. This figure clearly exhibits the possible gain in resistivity by using F-free tungsten as low resistance liner instead of the classical TiN material. Indeed, for thickness ranging between 3 and 5 nm (e.g. the standard thickness for TiN liner) the resistivity of the W liner is at least 60% lower than the one of TiN (around 200 μΩ.cm for W film vs. 600 μΩ.cm for TiN). Even for higher thicknesses (15 – 40 nm), the resistivity of TiN films remains greater than the one of thinner W films.

Since thin films of tungsten can be deposited either as an equilibrium phase with a body-centered-cubic structure denoted α-W of low electrical resistivity or as a metastable phase with an A15 (cubic) structure with high values of resistivity (denoted β-W) [24,17], the crystallographic phases of the F-free tungsten film have been studied by X-ray diffraction (XRD) measurements. The Fig. 3 shows the in-plane XRD pattern obtained for a 10 nm thick F-free W film. The inset table reproduces the calculated lattice parameter for each diffraction peak identified.

In the 2 θ range 30–100°, 3 diffraction peaks can be distinguished. Thanks to a modeling of the experimental spectrum, these peaks have all been attributed to the tungsten α-phase. The peak located at 38.7° matches with the {1 1 0} planes while peaks located at 69.7° and 82.1° correspond to {2 1 1} and {2 2 0} planes, respectively. Thus, the as-deposited F-free W film exhibits the lowest electrical resistivity phase: α-W. The calculated lattice parameter (from experimental data) is about

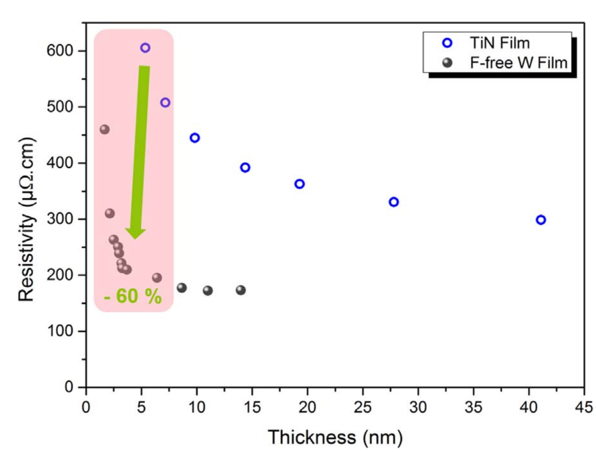

Fig. 2. Resistivity of F-free W (solid circles) and TiN films (open circles) as a function of thickness in the as-deposited state.