Effective Defect Control in TiN MHM Cu/low-k DD Process

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TiN metal hardmask was successfully integrated into DD Cu/low k metallization and has been accepted by 28nm and beyond technology nodes, where ultralow-k materials are highly required. However, time-dependent "TiFx" defects growing after fluorocarbon plasma DD etching challenge the process integration [1]. It is well known that these defects are triggered on TiN by CFx-based plasma with the following exposure in air. Different approaches were employed to overcome this problem including post-etch queue time control, N_2 purge of ambient, post-etch treatment (PET), etc [2]. In this work, *in situ* "N_2 plasma cleaning" method has been developed providing effective defect control in TiN MHM Cu/low-k DD process.

The growth mechanism of TiN HM defects is not fully understood. But many authors refer to TiFx residue as a cause of these defects. N_2-PET cleaning was employed and optimized highly reducing TiFx residue with no low k damage and productivity concerns.

MHM DD processing was carried out in a capacitively-coupled RF-plasma reactor. Pristine TiN wafers were used to study F specie content on surface at different CFx etch and N_2-PET plasma conditions by using XPS, SLIC (static leaching IC), Auger spectroscopy, defect review SEM and other analytical techniques. It was found by XPS that F-Ti bonds are the main contributors to fluorine content on post-etch TiN HM which are likely responsible for "TiFx" defects. Fig.1 shows strong gain in N_2 plasma TiN surface defluorination with exposure time, lowering pressure and increasing substrate temperature. SLIC data show that N_2-PET can reduce F content in TIN more than 10 times which correlates with XPS results (Fig.2a). Defect analyses on TiN HM DD pattern after etch with no PET showed lots of defects observed at 3 hour Q-time. However, no defects were found even at 24 hour Q-time, if DD process was completed with N_2-PET (Fig.2b). EELS analysis performing on DD pattern showed $\leq$1nm low k damage added by the optimized N_2-PET cleaning. The mechanism of N_2-PET cleaning was also in focus of this study and will be discussed. We consider N_2-plasma TiN HM defluorination as more effective PET and with no low k damage compared to H_2, H_2/N_2, NH_3 and CH_4 PETs [2]. The process has been successfully tested on Lam's Flex^{TM} FL etcher.

In this work, we also developed an alternative approach in preventing TiFx defect growth. Pristine TiN films were exposed in CF_4/C_4F_8/Ar plasma with different CF_4:C_4F_8 flow ratios. C and F depth profiles were measure by AES (Fig.3); C and F chemical states (bonds) were measured by XPS (Fig.4). Both methods show that CFx polymeric film was grown up on TiN with thickness ~3nm (AES), if flow ratio approaches 1:1. We assume CFx polymer can encapsulate TiN surface from being exposed in ambient. The following up test showed that no defects were found by SEM at this condition even at 24 hours Q-time (Fig.5). Defects appeared when the flow ratio was increased, for example up to 3:1 and more. The strong TiN fluorination (F-Ti bonds) and almost no polymer (F-CFx bonds) were detected by XPS (Fig.4), and grown defects observed by SEM (Fig.5). A similar approach with passivation of TiN surface but by using CH_4 plasma was demonstrated in [3].

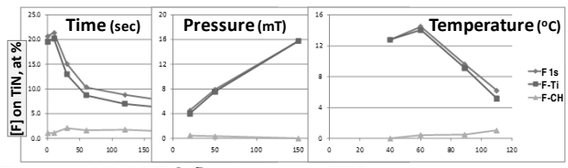

Figure 1: N2-PET defluorination on TiN versus time, pressure and temperature collected by XPS.

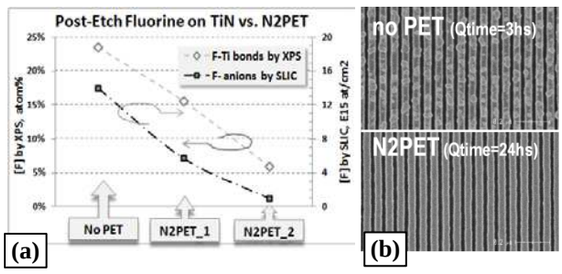

Figure 2: XPS and SLIC analyses results on blanket TiN - (**a**) and grown defects on MeHM DD pattern - (**b**) versus N2-PET.

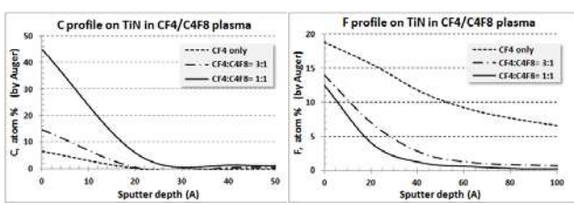

Figure 3: C, F depth profiles on TiN after CF_4/C_4F_8/Ar plasma exposure at different CF_4:C_4F_8 flow ratios (by AES).

XPS, at%	C, F chemical states on TiN in CF_4/C_4F_8 plasma			
CF_4:C_4F_8 flows	C-C, C-H	C-F2-CH2, CF3	F-CFx	F-Ti
CF4 only	6.4	0.7	-	38
CF_4:C_4F_8 = 3:1	7.6	3.1	-	27
CF_4:C_4F_8 = 1:1	11.0	27.0	42	3.3
Pristine TiN	8.7	0.9	-	0.3

Figure 4: Fluorine and carbon on TiN exposed in CF_4/C_4F_8/Ar plasma at different CF_4:C_4F_8 flow ratios (by XPS)

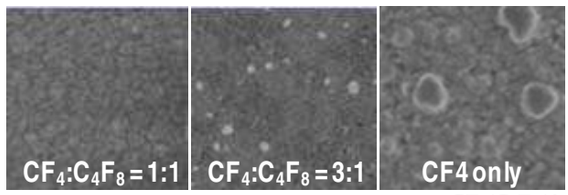

Figure 5: Defects on TiN at 24 hours Q-time after CF_4/C_4F_8/Ar plasma at different CF_4:C_4F_8 flow ratios (by top-view SEM)

We also investigated surface defluorination and fluorine cross-contamination effects on TiN blanket and TiN HM DD pattern in a FOUP as a result of F volatile species. As an example, TiFx defects appeared on post N2-PET DD pattern wafers stored in a FOUP together with non-PET wafer, but no defects found on the patterned wafers processed with N2-PET and stored in a separate FOUP.

References:

[1] Mei Qi Wang, et al, UCPSS proceedings, pp.75-76 (2006)
[2] N. Rosseme, et al, JVST B Vol.29, 011018 (2011)
[3] O. Joubert, et al, SSP Vol.187, pp.193-195 (2012)