Analysis of the composition of tantalum nitride in CMOS metallization trenches using parallel angle-resolved XPS

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We demonstrate the utilization of parallel angle-resolved X-ray photoelectron spectroscopy (pAR-XPS) as a useful tool to analyze ultrathin sputtered tantalum nitride (TaN) thin films in complementary metal-oxide-semiconductor (CMOS) trenches. The chemical composition of TaN was estimated by pAR-XPS using a Theta 300i from Thermo Fischer. An improved lateral resolution was achieved by analyzing periodic structures. The XPS data was correlated with transmission electron microscopy (TEM) in combination with energy-dispersive X-ray spectroscopy (EDX) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) data. The results show that the nitrogen content in the TaN thin films was about 6% higher at the sidewall compared with the top and bottom of the trench.

1 | INTRODUCTION

The progress in Moore’s law and the need for higher performance in nanoelectronic technologies resulted in the reduction of feature sizes in the back end of line (BEoL) of microchips. This shrinkage of interconnect structures is accompanied by an increase in the resistance-capacitance (RC) delay, which reduces the performance of the entire device. Hence, with advancing technology nodes, research is aimed toward improving BEoL materials and their properties.

This work focuses on the characterization of barrier layers in metallization trenches. Current industry standard uses a tantalum nitride (TaN)/tantalum (Ta) bilayer as barrier layer. The layer is typically deposited by physical vapor deposition (PVD), which can result in a poor sidewall coverage and elemental composition differences over the trench.\(^1\)\(^2\) The nitrogen content in TaN thin films affects the diffusion barrier performance and the sheet resistance of the thin film, which has a noticeable impact on the RC delay.\(^3\)\(^4\) Furthermore, it influences the crystallinity of the Ta layer deposited on top of it. Several publications describe a change from high resistive tetragonal \(\beta\)-Ta to low resistive body-centered cubic \(\alpha\)-Ta with increasing nitrogen content in the TaN interlayer.\(^5\)\(^-\)\(^7\)

For future technology nodes, it is therefore important to develop analysis methods that can be used to quantify current and future materials in small structures. In this paper, we show that parallel angle-resolved X-ray photoelectron spectroscopy (pAR-XPS) as a non-destructive analyzing method is suitable to analyze the sidewall of narrow CMOS trenches. Already in 1990, Oehrlein et al. used this technique to analyze the sidewall passivation layers formed by reactive ion etching in trenches with widths from 3 to 48 \(\mu\)m.\(^8\) More recently, Conard et al. conducted etch damage quantification on the sidewall of trenches by developing a model that distinguishes between the three parts: top, bottom, and sidewall of the trench.\(^9\) But so far, no studies are published that analyze the composition of the TaN PVD layer in trenches by pAR-XPS.

2 | MATERIALS AND METHODS

Three hundred-millimeter silicon wafers with trenches etched into the carbon-doped oxide dielectric (SICOH) were prepared. The trench structures have different dimensions, where all structures are periodically arranged on a field of 2 mm \(\times\) 2 mm to achieve the necessary
spot size for XPS analysis. The dimensions of the trenches as well as the overall layout of the structures are shown in Figure 1A. Line denotes the width of the trench and space the area between the trenches.

A 6-nm TaN thin film was deposited onto the structured SiCOH by DC magnetron sputtering in a standard Encore2™ chamber attached to an Endura2© cluster tool from Applied Materials Inc. The deposition of TaN was carried out at a DC power of 10 kW, a bias of 800 W, and argon and nitrogen flows of 4 sccm and 30 sccm, respectively. Angle-resolved XPS was performed in vacuo in a Theta 300i from Thermo Fisher Scientific that was attached to the Endura2© cluster. The system measures the electron signals in parallel for all angles, without tilting the sample. The measuring setup for pAR-XPS is illustrated in Figure 1B.

The base pressure of the analysis chamber was $3.5 \times 10^{-9}$ mbar and a high-resolution monochromatic Al Kα X-ray source was used with a spot diameter of 400 μm. The Ta4f, N1s, C1s, O1s, Si2p signals were acquired at a pass energy of 80 eV and with an angle ranging from 21.875° to 78.125°. The energy step size was 0.1 eV. The measurement was conducted at eight different points on the wafer to get sufficient data. The XPS signals were processed using CasaXPS. Charge calibration was conducted using the edge of the valence band spectrum because no adventitious carbon was detected. The spectra were fitted using Shirley background, and the Scofield sensitivity factors were applied.

The dimensions of the trenches were measured by atomic force microscopy (AFM) scans and are shown in Figure 2. The AFM measurements were conducted with the Dimension X3D in-line Atomic Force Microscope by Veeco Instruments Inc. A CNT500 tip from nanotools was used, and for each trench dimension, 96 trenches were measured. The resulting trench profiles were analyzed with the software μsoft analysis, where the profiles were aligned and corrected

**FIGURE 1** (A) Layout and dimensions of test pattern. (B) Parallel angle-resolved X-ray photoelectron spectroscopy (pAR-XPS) setup

**FIGURE 2** Trench sizes measured by atomic force microscopy (AFM): 50 nm, 100 nm, and 200 nm line width
regarding the used tip size (29 nm) in order to get the correct dimensions of the trenches.

With the measured trench sizes, a model was developed that correlates the angles in pAR-XPS with the trench area of the XPS signals. Figure 3 shows the angles with the corresponding top, sidewall, and bottom fraction for 50 nm × 50 nm and 100 nm × 100 nm trenches.

The XPS data were verified by transmission electron microscopy (TEM) in combination with energy-dispersive X-ray spectroscopy (EDX) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). A Tecnai G2 from FEI company and a ToF-SIMS 300R from IONTOF were used for the TEM and ToF-SIMS measurements, respectively. For both analysis methods, the trenches were filled with cobalt by electroplating. This enables the required stability of the trenches for TEM analysis and allows the separate analysis of top, sidewall, and bottom in the ToF-SIMS measurement. The EDX line scans were conducted using an acceleration voltage of 200 kV. The SIMS analysis was acquired on the 100 × 100 nm trenches. A bismuth (Bi1+) liquid metal ion gun (LMIG) was used as a primary source at 45° from the samples surface with an energy of 25 kV. The extraction lens is biased at −30 V to collect ejected species from the analysis area. Sputtering was achieved with 1 keV cesium ions (Cs+) at a 45° incidence angle.

3 | RESULTS AND DISCUSSION

All acquired spectra were quantified, and the ratio of nitrogen to tantalum was calculated for each angle and plotted in Figure 4. It can be seen that with decreasing angle, the N/Ta ratio increases. By applying the aforementioned model, it has been derived that lower angles represent the XPS signals from the sidewall and the top of the trench, whereas with increasing angle, the influence of the sidewall on the overall signal decreases. Keeping that in mind, from the data trend in Figure 4, it can be concluded that the sidewall of 50 nm and 100 nm trenches has a higher nitrogen content than the top of the trench.
In addition, the signals for nitrogen and tantalum were summed over all angles. The plot of the summed N/Ta ratios (Figure 5) shows an increase of nitrogen content with decreasing space dimensions. That means the size of the space, which equals the top of the trench, has an impact on the detected nitrogen concentration and further proofs a lower nitrogen concentration on the top of the trench. The lower N/Ta ratio for a line width of 100 nm compared with wider trenches (200 and 300 nm) could be due to the shadowing effect of smaller trenches. This shadowing effect results in a less detected signal from the sidewall when summing the signal and hence results in higher N/Ta ratios for wider lines.

Internal simulations on TaN deposition in trenches state that the nitrogen content in the bottom and top of the trench is similar to the composition on a blanked wafer. With this assumption, the N/Ta ratio of a 6-nm blanked wafer was used to calculate the composition of sidewall, top, and bottom of TaN in the trenches. The applied equation is given as following, where a and b represent the fractions of the XPS signal for sidewall, top, and bottom:

\[
\text{Signal}_{\text{all}} = a \text{Signal}_{\text{sidewall}} + b \text{Signal}_{\text{top + bottom}}
\]

The calculation results in an overall N/Ta ratio of 0.64 on the sidewall and 0.49 on top and bottom. This gives nitrogen concentrations of 39% and 33% for the sidewall and top + bottom, respectively, for both 50 nm and 100 nm trenches. Hence, the nitrogen content in the TaN thin films is 6% higher at the sidewall compared with the top and bottom of the trench.

For verification of the XPS results, TEM in combination with EDX was conducted. Figure 6 shows the EDX line scan data. The ratios of N/Ta on top, bottom, and sidewall of the trench were calculated and compared with the XPS data. The EDX line scan on top and bottom results in N/Ta ratios of 0.52 and 0.55, respectively. The sidewall shows a N/Ta ratio of 0.6. Those values are in good agreement with the N/Ta ratios estimated with pAR-XPS of 0.64 and 0.49.

In comparison with EDX where the measurement data can only be acquired from certain points, ToF-SIMS is able to provide the analysis from the entire trenches (top-down analysis) and/or cross-sectional analysis. The sputter area of the ToF-SIMS analysis was 300 × 300 μm and the acquisition spot was 100 × 100 μm to avoid effects caused by the sidewalls of the sputtered area. The resulting profile is shown in Figure 7. The top and bottom of the trench are clearly visible in the profile.

**FIGURE 6**  Energy-dispersive X-ray spectroscopy (EDX) line scans and transmission electron microscopy (TEM) for 100 × 100 nm trenches.
We compared the acquired high-resolution mass spectrums of NH\textsuperscript{-} and Ta\textsuperscript{-} from 100 \times 100 nm trenches of three different regions: the top sides, the sidewalls, and the bottom sides. The NH\textsuperscript{-} signal was used instead of the N\textsuperscript{-} signal due to its better sputter yield and the higher sensitivity. To calculate the ratio between NH\textsuperscript{-} and Ta\textsuperscript{-}, we used the area under each curve in the mass spectra.

The resulting N/Ta ratio equals on top and bottom with a value of about 0.1, and the sidewall shows a ratio of approximately 0.31, which is three times higher compared with bottom and top. As the ToF-SIMS data were not calibrated by reference samples and no sensitivity factors were applied, it is not possible to compare the resulting numbers directly to the XPS and EDX data. However, the ToF-SIMS data in combination with the EDX results confirm the assumption that bottom and top of the trench have the same composition. Furthermore, it shows that the nitrogen content in the sidewall is clearly higher compared with top and bottom. This confirms that our model for calculating the ratios of nitrogen to Ta in pAR-XPS for top, bottom, and sidewall is valid.

For future technology nodes, those results are of high importance. As there are little alternatives to the currently used TaN/Ta bilayer as diffusion barrier, research still aims toward improving those materials. Most research has been done on blanket wafers, but as trench sizes are getting smaller, the material properties of patterned structures become more and more important. As stated at the beginning of this paper, the composition of TaN has an impact on the crystallinity of the overlaying Ta and on the RC delay in interconnects. By applying this technique, the composition of TaN in CMOS trenches can be analyzed without breaking vacuum and without sample preparation. This allows for a better understanding of local material properties and hence further performance improvement of barrier layers and the development of future interconnects.

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