Properties of TaN Thin Films Produced Using PVD Linear Dynamic Deposition Technique*

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(Received 24 June 2008; Accepted 5 January 2009; Published 4 April 2009)

Thin tantalum nitride layers were sputtered using Linear Dynamic Deposition (LDD) implemented in the 10 cathode TIMARIS Physical Vapor Deposition (PVD) sputtering equipment from Singulus Nano Deposition Technologies. During the deposition, the wafer is moved in a linear path underneath a rectangular cathode/target which remains stationary and sputtering is performed using a reactive N$_2$/Ar gas mixture. For investigation of the properties of the TaN layers, layers were deposited with three different final thicknesses of 10, 20 and 50 nm on 200 mm SiO$_2$/Si wafers. Also, the influence of various process parameters like pressure in the deposition chamber and nitrogen flow during the deposition was investigated. The uniformity of the sheet resistance (Four Point Probe), the surface roughness (Atomic Force Microscopy), the thickness uniformity (X-Ray Reflectometry and Transmission Electron Microscopy), the stoichiometry (X-Ray Photoelectron Spectroscopy), and the crystallographic structure (X-Ray Diffraction) of the deposited films were characterized. For the deposited layers, a resistivity in the range from 337 $\mu\Omega$cm to 526 $\mu\Omega$cm was achieved for layer thicknesses of 50 nm and 10 nm, respectively. The statistical spread ($1\sigma$) of the resistivity within the wafer is in the range of 1% and below. The TaN layers also show excellent thickness uniformity below 0.6% ($1\sigma$) and a very smooth surface with roughness below 0.4 nm. According to XPS analysis, the stoichiometry of the thin films was found to be independent of the layer thickness resulting in a tantalum nitride compound with a stoichiometry of TaN. While the stoichiometry of a TaN compound is unaffected, the proportion of the phases and the crystallinity are strictly coupled with the deposition conditions. Very good agreement between different analytical methods with respect to the interrelation of physical properties like sheet resistance of the layers, stoichiometry between Ta and N in the layers, as well as crystallographic structure was achieved. [DOI: 10.1380/ejssnt.2009.277]

Keywords: Tantalum nitride; Thin films; PVD; Resistivity; Stoichiometry

I. INTRODUCTION

There is an ongoing need to enhance processes and to introduce new materials to enable further down-scaling of CMOS devices. New techniques are required to ensure an excellent controllability of the deposition process for thin films resulting in layers with outstanding properties like e.g. layers thickness homogeneity, surface roughness or sheet resistance uniformity. The poly-silicon gate electrode [1] has to be replaced by thin metal layers with better thermal stability and aligned barrier properties. In terms of these requirements, TaN is a promising candidate.

In numerous publications it has been shown [2–5] that the properties of thin tantalum nitride layers depend very strongly on the deposition technique and the process conditions used during deposition. In dependence on the ratio of N$_2$/Ar gas mixture used during the sputter processes the deposited thin TaN layers are identified to have different phases [6, 7], different stoichiometry and crystallinity which will result in deviation in electrical sheet resistance.

Because of the critical dependence of the layer properties on the process parameters for each specified equipment, the characterization of tantalum nitride thin layers produced in the Linear Dynamic Deposition (LDD) TIMARIS Physical Vapor Deposition (PVD) sputtering equipment was performed.

II. EXPERIMENTAL PROCEDURES

The deposition of tantalum nitride thin films was performed on Si wafers with a diameter of 200 mm covered with 100 nm SiO$_2$. The thin layers were sputtered in a
Linear Dynamic Deposition (LDD) system implemented in the 10 cathode TIMARIS Physical Vapor Deposition (PVD) sputtering equipment from Singulus Nano Deposition Technologies [8]. The LDD method is based on the technical solution in which a wafer is moved in a linear and cyclical path under a stationary cathode during the sputter processes (Fig. 1). The TaN layers were deposited from a metallic Ta target using a reactive dc-magnetron process. To find the optimal conditions for depositing of stoichiometric TaN with a Ta to N ratio of one, a calibration of the sputter condition was performed. The optimum N\textsubscript{2} partial pressure (i.e., N\textsubscript{2} flow) in the N\textsubscript{2}/Ar gas mixture was determined by an indirect method by checking the phase transformation from \(\beta\)-Ta to \(\alpha\)-Ta deposited on TaN indicated by a drop in the specific resistance (Fig. 2). This transformation point (working point) indicates stoichiometric TaN and depends on the sputtering geometry as well as on pressure and the power.

During the sputtering, the process parameters were varied to investigate their impact on properties of the deposited TaN thin films. The deposition of the TaN layers was performed at a power of 1.25 kW and a pressure of 1.1 \(\mu\text{bar}\), 1.9 \(\mu\text{bar}\), and 3.7 \(\mu\text{bar}\). For each pressure the calibration procedures were performed to determine the working point and the optimal nitrogen flow resulting in ratios of N\textsubscript{2} to Ar 47.5 sccm/82.5 sccm, 60 sccm/160 sccm, and 80 sccm/360 sccm, respectively. For the pressure of 1.9 \(\mu\text{bar}\) which was found to be optimal, films with three final thicknesses of 10, 20, and 50 nm were deposited for characterization of the deposited tantalum nitride layers. The layers were tested ex-situ in respect to uniformity of the sheet resistance using Four Point Probe (4PP), surface roughness by means of Atomic Force Microscopy (AFM), thickness uniformity by Transmission Electron Microscopy (TEM) and X-Ray Reflectometry (XRR). The stoichiometry was determined using X-Ray Photoelectron Spectroscopy (XPS) and the phase content by using X-Ray Diffraction (XRD). Detailed information regarding metrology was placed in Table I.

III. RESULTS AND DISCUSSION

The deposition of thin film using the LDD technique results in layers with very good resistance uniformities within the 200 nm wafers (Fig. 3(a)). The statistical spread (1\(\sigma\)) is lower than 1.2% and reaches the value of 0.8% for layers with a thickness of 20 nm. The resistivity of TaN deposited with different thicknesses for identical deposition conditions shows a clear dependence on the film thickness (Fig. 3(a)). The resistivity ranges from 337 \(\mu\Omega\text{cm}\) for 50 nm thick film to 526 \(\mu\Omega\text{cm}\) for 10 nm thick film. This kind of behavior was reported for metallic thin layers like e.g. Cu or Ta [9], showing that the resistiv-
If the thickness of the film is smaller than 20 nm, the TaN layer relating to the thickness of deposited films. The reason is the reduction of the long range order and contributions, etc. The reason is the reduction of the long range order and contributions, etc.

### TABLE II: Proportion of the Ta-N phases and stoichiometry

| Phase proportion (%) from XPS | XPS | XPS |
|-----------------------------|-----|-----|
| Ta2N cubic TaN              | 28  | 53  |
| Ta5N5                        | 20  | 0.93|
| Ta/N                         | 24  | 0.97|

The thickness of the film is smaller than 20 nm, the TaN layer relating to the thickness of deposited films. If the thickness of the film is smaller than 20 nm, the resistivity increase is about 50% and shows an exponential rise. In Fig. 3(b) a bulk resistivity of the tantalum nitride films equals about 200 $\mu$Ωcm and was calculated using $\lambda = 25$ nm as reported by Rossnage [4]. Lowest difference in resistivity and sheet resistance is seen for the 50 nm TaN. For the film thickness of 20 nm, the resistivity reduces from 400$\mu$Ωcm to the bulk resistivity of 200 $\mu$Ωcm confirming the theoretical prediction. The resistivity of the 10 nm thick film after $\lambda$ corrections declines as well and reaches the bulk resistivity of about 200 $\mu$Ωcm.

Beside of the scattering events, also degrees of the crystallization and distribution of crystallographic phases between the layers with 10 and 50 nm is only about 0.2 nm. Although the numerical difference is not so high, a change of the surface topology is noticeable (Fig. 4(a)). The layers with a thickness of 50 nm show well formed grains with a grain size bigger than that one in the layers with 20 nm or 10 nm thick tantalum nitride film. The bigger size of the grains lowers the density of the grain boundaries and contributes to a higher conductivity of the TaN films.

As reported in the literature [10–13], Ta-N systems are very complex and show numerous stable and metastable phases which exhibit different physical properties like different sheet resistance, stoichiometry, etc. Additionally, thin TaN films show a mixture of different crystallographic phases with a high sensitivity to the deposition conditions. Therefore, an analysis of the composition and the phases formed during the deposition of the tantalum nitride play a crucial role for the explanation of the properties of the deposited layers.

The XRD spectra of the TaN films deposited with the thicknesses of 20 nm and 50 nm are shown in Fig. 5. The phase identification was performed using the “X’Pert High score” software from PANalytical having an embedded XRD database PDF2. Independent from the layer thickness in the deposited thin films the same compounds (Fig. 5) cubic TaN, hex-Ta2N, hex-Ta5N6, and hex-TaNO were detected. The result of the phase identification correlates very well with the literature statement where only cubic TaN phase formed in nature, hex-Ta2N, hex-Ta5N6 and Ta3N5 were found to be stable [11]. The sample with 50 nm thick TaN shows narrower peaks (smaller full width at half maximum) related to compound phases which are more crystalline compared to the sample with 20 nm thickness. A broadening of peaks in the spectrum for 20 nm TaN may be attributed to a higher content of the amorphous phase. A similar structure of tantalum nitride thin films was reported by Nie [12]. Namely, the TaN deposited by reactive radio-frequency magnetron sputtering appoint in the film different phases of metallic Ta, cubic Ta(N) and hex-Ta2N. The different phases and ratios to each other were depending on the deposition conditions. A texture of the deposited layer is a mixture of locally crystallized zones with varying randomly spacing and orientation, and amorphous regions.

To determine peak ratio for different phases in the layers and the ratio between the tantalum and the nitrogen, another technique like XPS was applied. The XPS characterization was performed after removing a few nanometers of the tantalum nitride film from the sample surface to avoid an influence of the surface contamination and to perform the characterization inside the thin layer. In Fig. 6(a) typical XPS spectra of Ta 4f, Ta 4p and N 1s determined for the tantalum nitride layers deposited in the LDD TIMARIS system are shown. In the XPS spectra, the different phases of metallic Ta, cubic Ta(N) and hex-Ta2N are clearly resolved. The Ta-N system is very complex and shows numerous stable and metastable phases which exhibit different physical properties like different sheet resistance, stoichiometry, etc. Additionally, thin TaN films show a mixture of different crystallographic phases with a high sensitivity to the deposition conditions. Therefore, an analysis of the composition and the phases formed during the deposition of the tantalum nitride play a crucial role for the explanation of the properties of the deposited layers.

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FIG. 4: (a) AFM micrographs of the surface of the TaN films with thicknesses of 10 nm, 20 nm, and 50 nm. (b) Surface roughness of the TaN layers measured by AFM.

FIG. 5: XRD patterns of tantalum nitride films deposited with a thickness of 20 nm, and 50 nm. GIXRD, incidence angle omega 1°, \( \lambda = 1.5405 \) Å.

peak form are comparable and are independent from the layer thickness appointing the same stoichiometry close to one between tantalum and nitrogen (Table II). Although, the stoichiometry of Ta:N is unaffected by the film thickness, the proportion of the phases in the samples is varying with the layer thickness. The determination of the nature of the formed phases and their proportion in the films were determined after deconvolution of the Ta 4f/4 peak. The fitting procedures reveal three components allocated to binding energies of 22.9 eV, 23.6 eV, and 25.7 eV. The first two energies are attributed to the hex-Ta2N and cubic TaN phases, respectively, giving an excellent correlation with the data reported in the literature [14]. The third peak at 25.7 eV has not been found in the literature. However, on the basis of the phase identification from XRD it could be ascribed to the hex-Ta5N6 phase. The results of the determination of the phases proportions detected by XPS (Table II) show that the sample with the thicker film has the lower quantity of cubic TaN and a higher abundance of hex-Ta2N and hex-Ta5N6 compounds compared to the samples with 20nm TaN. From the XRD spectrum (Fig. 5) a low intensity of the TaN peak at 41° (2 Theta) for the 50 nm thick sample is visible in relation to the clearly visible TaN intensity for the 20 nm film. In addition to the peaks attributed to the cub-TaN, hex-Ta2N, hex-Ta5N6, peaks appear between 52° and 55° (Fig. 5). The position of the peaks is characteristic for the TaNO and is in agreement with the XRD pattern of TaNO reported by Armytage [15].

Using analytical methods like Auger spectroscopy, X-Ray Reflectometry and TEM it was proven that the TaNO compound is located at the surface of the TaN film confirming the results published in [16]. Auger concentration depth profiles (Fig. 7) shows an onset of the tantalum signal being in an oxidation state appoints the additional layer on the surface of TaN. In Fig. 8(b), a TEM cross section of the sample with 10 nm thick tantalum nitride film showing very well formed film on the top of TaN is presented. The analysis of the TEM images of all samples with different final thicknesses for different deposition conditions yields always the layer stack with the TaNO top layer with thickness ranges between 1.5 nm and 2.0 nm. Also from the XRR modelling and analysis, the assumption of a TaNO/TaN/SiO2/Si layer stack was necessary to gain a suitable fit between experimental and simulated data. The density of TaNO found in the literature is 5.62 g/cm³ [17]. On the basis of the XRR results, the density of TaNO on the TaN ranges between 4.0 and 5.8 g/cm³ and no correlation between deposition condition and the density of the TaNO was found. The reason of the density variation could be e.g. oxygenation of the non-stoichiometric range of TaNO reported by Swisher and Read [18]. The thicknesses of layers both for TaNO film and TaN film determined from XRR and TEM correlate very well with each other (Fig. 9).

Taking into account an interface reaction between the tantalum nitride and the silicon dioxide, no interface layer was detected on the basis of TEM (see Fig. 8) and XRR which is in an accordance with the literature predictions [19] showing TaN island formation without an interfacial reaction at the beginning of the reactive DC magnetron sputtering of thin TaN films on silicon dioxide.

For the determination of the properties of tantalum nitride film from the LDD TIMARIS depending on the pressures used during the film fabrication, the deposition with pressures of 1.1 µbar, 1.9 µbar, and 3.7 µbar was performed. Figure 10 shows the bulk resistivity of the 20 nm thick tantalum nitride films deposited at different pressures calculated with the free mean path of 25 nm for the conductive photoelectrons. Each layer characterized the statistical spread of the resistivity lower than 1% and the resistivity in the range of about 200 µΩcm. The bulk resistivity of the layer deposited at 1.1 µbar is 220...
FIG. 6: XPS spectra of (a) Ta 4f and (b) Ta 4p, N 1s acquired for the tantalum nitride films deposited with the target thickness of 20 nm and 50 nm.

TABLE III: Results of the characterization of the 20 nm thick tantalum nitride films deposited at different pressures.

| N₂/Ar Pressure Phase proportion from XPS (%) | XPS 4PP | XRR |
| (sccm) (µbar) | Ta₂N cubic TaN Ta₅N₆ | Ta/N Resistivity (µΩcm) | Thickness (nm) | 1σ (%) |
|---------------|-----------------|------------------|-----------------|------|
| 47.5/82.5     | 1.1             | 31               | 50              | 20   | 0.98 | 227 | 19.7 | 0.3% |
| 60/160        | 1.9             | 29               | 52              | 19   | 0.90 | 198 | 19.6 | 0.2% |
| 80/360        | 3.7             | 28               | 54              | 18   | 0.91 | 186 | 20.0 | 0.3% |

FIG. 7: Auger concentration depth profile at the surface of 50nm thick tantalum nitride film.

μΩcm, for the layers deposited at 1.9 µbar and 3.7 µbar is 192 µΩcm and 184 µΩcm, respectively. The difference between the resistivity at 1.9 µbar and 3.7 µbar is only 5% and the value of the resistivity at 1.1 µbar comparing with 3.7 µbar is 20% higher. The variation of the bulk resistivity has its origin in the crystalline phase content of the deposited tantalum nitride. The same holds for the films deposited with different final thicknesses, although in the bulk of the TaN layers deposited at different pressures the same phases of cub-TaN, hex-Ta₂N, hex-Ta₅N₆ can be indicated. Also, the 1.5 nm thick TaNO film was detected at the surface of the TaN layers. In Fig. 11, XRD spectra of TaN films sputtered at 1.1 µbar and 3.7 µbar are shown. The film deposited at the higher pressure compared to the film deposited at the lower pressure reveals a lower intensity and narrower peak shape at 35° 2Theta. On this account, it could be concluded that the film deposited at the higher pressure has less amorphous part and the phases of the cubic TaN and hex-Ta₅N₆ embedded in the film are more crystalline. The higher portion of amorphous phase in the film deposited at 1.1 µbar could be a reasonable explanation for the rise of the resistivity.

An increase of the fraction of the cubic TaN phase (higher peak at 41° 2θ and 60° 2θ) is in accordance with the results of the phase determination achieved from XPS (Table III), showing an increase of the quantity of cubic TaN phase and a decrease of the hex-Ta₂N and hex-Ta₅N₆ with increasing deposition pressure. The estimated ratio between the tantalum and nitrogen within the TaN films extracted from XPS-data (Table III) is 0.98, 0.90 and 0.91 for the layer deposited at the pressures 1.1 µbar, 1.8 µbar and 3.7 µbar, respectively. The film show excellent thickness uniformities within the wafer with values lower then 1% and final thickness agrees well thickness with the required final thickness (Table III).

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FIG. 9: Thickness of the TaNO/TaN layer determined using XRR and TEM. 1σ values placed at the top of the XRR bar denote the statistical spread of the thickness within the wafer measured for 25 points.

FIG. 10: Resistivity of 20 nm thick tantalum nitride films deposited at different pressures.

FIG. 11: XRD spectra of the 20 nm thick TaN films deposited at the pressures of 1.1 µbar, and 3.7 µbar. GIXRD, incidence angle: θ = 1.5°, λ = 1.5405 Å.

IV. CONCLUSIONS

In this study, thin tantalum nitride films deposited in the LDD TIMARIS tool were analyzed. The composition and properties of the TaN layers were investigated in relation to the thickness of the deposited layers and the various pressures used during the deposition.

It was found that independent from the deposition conditions, films are indicated by very low surface roughness with RMS-values in the range of 0.2 nm to 0.6 nm. Very good uniformity of the resistivity and the film thickness within the wafer (statistical spread close or below 1%) were found. The gained bulk resistivity of the deposited TaN is in the range of about 200 µΩcm making it a feasible material for the multichip module technologies [20].

Acknowledgments

The authors would like to thank D. Klemm for AES measurements.

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