Development of PECVD WNₙ ultrathin film as barrier layer for copper metallization

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Abstract

A PECVD process for WNₙ deposition was developed to deposit ultrathin films of 10-nm thickness using a WF₆–N₂–H₂ gas mixture. This paper deals with the influence of several process parameters such as temperature, RF power and gas flows on the deposition rate. For a stable deposition process of ultrathin films, a low deposition rate with controllable parameters is required. All deposited WNₙ films have a X-ray amorphous microstructure and the fluorine content in the film is very low. Their electrical resistivity is around 200 μΩ cm and almost independent of the film composition and the film thickness. This is why it is a promising diffusion barrier.

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1. Introduction

New metallization technologies will be required, as critical semiconductor device dimensions shrink. One necessity of these future metallizations is an extremely thin diffusion barrier that will be compatible with copper. Tungsten nitride as a refractory metal nitride, is able to fulfil the requirements of barrier properties due to its low self-diffusion and the absence of any reaction with copper [1]. Therefore this paper is focused on the PECVD process for ultrathin WNₙ layers and its influence on the WNₙ film properties.

2. Experimental

The technical conditions to create WNₙ CVD is a tungsten CVD chamber on a commercial cluster...
tool Precision 5000 (Applied Materials), which provides the opportunity to integrate barrier and copper CVD. WN$_x$ films have been deposited by PECVD from WF$_6$–N$_2$–H$_2$ chemistry with thicknesses of about 10, 30 and 50 nm onto 150 mm blanket silicon substrates with a thermal oxide layer. The influence of temperature, rf power and WF$_6$ gas flow on the deposition rate was investigated. The deposition temperature was varied from 350 to 450 °C. The RF power was decreased from 200 to 50 W. The WF$_6$ (diluted in Ar) partial pressure was varied between 1.3 and 16 Pa. At a constant WF$_6$ flow-rate, the influence of the gas ratio components (H$_2$–WF$_6$, N$_2$–WF$_6$ and H$_2$–N$_2$) on the film properties was investigated. The WN$_x$ films were characterised by the sheet resistance (four point probe measurement), film thickness (surface profilometer and AFM) and by XRD as well as TOF-SIMS, AES and RBS of selected samples.

3. Results

3.1. Deposition process for ultrathin films

Initially we installed a basic process with the following process parameters: $T = 400$ °C (susceptor), $P = 670$ Pa, H$_2$–WF$_6$ = 40, N$_2$–WF$_6$ = 10 and rf power = 100 W [2]. Before the deposition step, a H$_2$ + N$_2$ plasma treats in situ the substrate surface to obtain a uniform smooth film [3]. Starting out from this process, we varied temperature, rf power and WF$_6$ gas flow to achieve lower deposition rates. These parameters have various strong influences on the deposition rate. Moreover the deposition pressure and the plasma power are likely to introduce nonlinearity because of the plasma enhancement [4].

Under the investigated process conditions, the deposition rate was approximately 120 nm/min and almost completely independent of temperature. But the film uniformity is improved at higher temperatures. At temperatures below 400 °C particles were predominantly at the edge of the wafer. No deposited film was achievable at 300 °C, only particles were visible.

The deposition is mainly driven by plasma. In the range between 200 and 50 W, the dependence of the deposition rate is nearly linear. The deposition rate decreases by 50% if the rf power is dropped. This decrease in deposition rate is due to smaller amounts of active species forming with lower rf power. Electrical resistivity is slightly affected by the plasma in the above range. It increased by 20 μΩ cm (Fig. 1).

It has been reported that WF$_6$ flow affects the deposition rate used in WF$_6$–NH$_3$ chemistry [5]. We established a strong relationship between the deposition rate and the WF$_6$ total flow. Fig. 2 shows this dependence at 100 W and at 55 W rf power. The deposition rate decreases by half if the flow-rate is diminished by a factor of 3.

The pressure influence was not investigated. The chamber configuration limited the smallest stable pressure to 335 Pa. Ganguli et al. [4] reported the relationship between the deposition rate and chamber pressure. Pressures below and above the deposition rate peaking at 670 Pa result in decreased deposition rates.

Deposition rates of 20 nm/min were achievable with $T = 400$ °C, rf power = 55 W, $P = 335$ Pa and a WF$_6$ partial pressure of 1.5 Torr. Under these process conditions we deposited reproducible WN$_x$ films of 10-nm thickness (Table 1).
3.2. Characterization of WN$_x$ films

The sheet resistance and nonuniformity of WN$_x$ films was calculated based on an 81 point measurement of the four point probe. Despite the range of stoichiometry and film thickness of as-deposited films, their resistivities are located in a relatively narrow range between 190 and 200 $\mu\Omega$.
Table 1
Properties of 50- and 10-nm thick films \((T = 400 ^\circ C, P = 335 \text{ Pa}, H_2-WF_6 = 80, H_2-WF_6 = 80)\)

<table>
<thead>
<tr>
<th></th>
<th>Thin films</th>
<th>Ultrathin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness (nm) by AFM</td>
<td>56.9</td>
<td>12.0</td>
</tr>
<tr>
<td>Sheet resistance ((\Omega/\text{sq.}))</td>
<td>39.7</td>
<td>183.7</td>
</tr>
<tr>
<td>Electrical resistivity ((\mu\Omega\ cm))</td>
<td>215.6</td>
<td>218.6</td>
</tr>
<tr>
<td>Within wafer uniformity (%) 1(\sigma), 5 wafers</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Wafer to wafer uniformity (%) 1(\sigma), 5 wafers</td>
<td>0.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Surface roughness rms (nm)</td>
<td>0.632</td>
<td>0.378</td>
</tr>
</tbody>
</table>

cm. Only a very low gas flow ratio of \(H_2-WF_6 = 25\) resulted in a higher resistivity of \(385 \mu\Omega\ cm\). However, a ratio of 30 is sufficient to decrease the value to \(210 \mu\Omega\ cm\). The effect of ratio \(N_2-WF_6\) at higher \(H_2-WF_6\) ratios is negligible, but at the low ratio of 30 the influence on resistivity is stronger (Table 2). The narrow range of electrical resistivity may indicate that the microstructure of the WNx films has an amorphous-like nature. Proof of this is confirmed by grazing incidence XRD examinations (Fig. 3). The patterns show only a broad hump with the copper diffraction peaks. The electron diffraction pattern of a tungsten rich sample (WN4) also exhibits a diffuse diffraction ring (Fig. 4).

Table 2
Influence of different \(N_2\) gas flows at two \(H_2-WF_6\) ratios on resistivity, stress and \(N/W\) ratio

<table>
<thead>
<tr>
<th>(H_2-WF_6)</th>
<th>(N_2-WF_6)</th>
<th>Thickness (nm)</th>
<th>(\rho) ((\mu\Omega\ cm))</th>
<th>Stress (MPa)</th>
<th>N/W RBS not tilted</th>
<th>N/W RBS tilted</th>
</tr>
</thead>
<tbody>
<tr>
<td>WN1</td>
<td>30</td>
<td>20</td>
<td>25.3</td>
<td>209.4</td>
<td>1284</td>
<td>0.375</td>
</tr>
<tr>
<td>WN2</td>
<td>30</td>
<td>80</td>
<td>30.8</td>
<td>232.5</td>
<td>1452</td>
<td>0.46</td>
</tr>
<tr>
<td>WN3</td>
<td>30</td>
<td>110</td>
<td>34.8</td>
<td>285.6</td>
<td>1547</td>
<td>0.93</td>
</tr>
<tr>
<td>WN4</td>
<td>80</td>
<td>20</td>
<td>30.8</td>
<td>190.6</td>
<td>682</td>
<td>0.38</td>
</tr>
<tr>
<td>WN5</td>
<td>80</td>
<td>80</td>
<td>34.1</td>
<td>204.0</td>
<td>1080</td>
<td>0.54</td>
</tr>
<tr>
<td>WN6</td>
<td>50</td>
<td>140</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. GI XRD patterns of 10-nm WN5 and WN6 films covered by CVD Cu (curves are shifted vertically for clarity).
The impurity content was studied by AES depth profiling and TOF SIMS depth profiling. Elements analyzed were W, N, F, C, O and Si. Among them, W, N and F are incorporated in the film due to process gases while Si and O are analyzed to determine the WN$_x$–SiO$_2$ interface. Two different H$_2$:N$_2$ gas ratios (WN4, WN5 see Table 2) are analyzed while H$_2$ flow and WF$_6$ flow remain fixed. Higher N$_2$ flow results in higher N$_x$ content in the film. AES analysis of these films showed O and F incorporation below detection limits of 0.5 at.% for F and 1 at.% for O. Especially the F content in these films is very low compared with other publications [4] [6], and [7]. TOF SIMS has a higher resolution and O and F were detected. F is continuously distributed within the WN$_x$ layer as well as at the WN$_x$–SiO$_2$ interface.

The N:W ratio was determined by RBS. It is difficult to determine this ratio if WN$_x$ is deposited on SiO$_2$, because the signals of N and O cannot be separated. The ratio is evaluated by the signal plateau of W and RUMP simulation standardized with α-W. But this kind of evaluation presupposes that only N as a light component is included in the film. The above AES measurements of the films showed that this is a good assumption. Samples are measured in two ways, not tilted and tilted. The results differ from each other but show the tendency of a higher nitrogen content in the film with the higher nitrogen flow. The measured films were around 30-nm thick. With a tilted sample, a higher bulk volume was recorded with higher information density and improved accuracy (Table 2).

The thickness and surface roughness is measured by AFM. The surface roughness will be smoother with thinner films. For 10-nm thick films, rms = 0.378 nm and $R_{\text{max}}$ amounts to 16% of the film thickness.

WN5 and WN6 were used for annealing and Cu anneal experiments. The samples were annealed in hydrogen and nitrogen ambients at 450 and 550 °C. This was to evaluate the effect of different annealing ambients for the electrical characterization of barrier stability by using CV and BTS measurements at MOS structures. After annealing at 550 °C in nitrogen ambient no change in the
Fig. 5. Changes in electrical resistivity of 50 nm WN5 and WN6 films by annealing in N$_2$ and H$_2$ ambient.

electrical resistivity of WN$_x$ was observed. But it decreases down to 50 $\mu$Ω cm when annealing in a hydrogen ambient (Fig. 5). The hydrogen was found to be able to reduce the WN$_x$ to pure $\alpha$-W, whereas nitrogen annealing did not influence the barrier properties. This is confirmed by GI XRD measurement (Fig. 6).

The annealing of WN$_x$ with Cu cap layer (80 nm) hydrogen ambient resulted in Cu agglomeration and giant grain growth of some Cu grains (Fig. 8). After annealing at 450°C some giant grains and some small holes in the Cu surface are visible. The XRD results determined that Cu is effective in

Fig. 6. GI XRD patterns of 50-nm WN5 films as-deposited and after annealing in N$_2$ and H$_2$ ambient (curves are shifted vertically for clarity).
delaying the reduction of WN₅ at 450 °C. The SEM picture of Cu surface after annealing at 550 °C shows more giant grains and agglomeration of the Cu. Large areas of the WN₅ surface are uncovered. This also lead to a reduction of WN₅ to W at 550 °C, like the XRD spectra confirmed (Fig. 7).

4. Conclusion

We have optimized the PECVD process using WF₆–H₂–N₂ chemistry for the deposition of 10-nm WN₅ films. Low deposition rates are required to deposit ultrathin films with a reproducible process. The deposition rate is influenced by rf power, pressure and WF₆ gas flow. At low values of these process parameters a reproducible process was achievable. The deposited films have electrical resistivities in the narrow range between 190 and 230 μΩ cm, dependent on the N:W ratio. Films with the same composition but different thicknesses did not show any divergence in electrical resistivity. The amorphous-like microstructure of the film impedes grain boundary diffusion and is a highly advantageous structure for barrier films. The F content of the films is below the detection limit of 0.5 at.%.

The annealing in hydrogen ambient affects the barrier properties on account of the reduction of
WN$_2$ to pure α-W. Care has to be taken in choosing the annealing ambient for the investigation of barrier integrity because of the likelihood of N release in reducing ambients.

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References