A Tuneable Metal Gate Work Function Using Solid State Diffusion of Nitrogen

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Abstract

The work function of a metal gate electrode has been adjusted by the incorporation of nitrogen at the metal-dielectric interface. The nitrogen was introduced using solid state diffusion from an over-stoichiometric TiN$_{1+x}$ layer. RBS measurements demonstrate that up to 35 at% nitrogen can be diffused into a 10nm Ta layer from the TiN layer and that the diffused concentration increases with anneal temperature. The effects of nitrogen incorporation upon the gate work function were studied for tantalum on Al$_2$O$_3$ and for molybdenum on SiO$_2$ and on Al$_2$O$_3$. The work function of tantalum is slightly affected by the presence of the TiN exhibiting a change of -0.08 ± 0.05eV, comparable to the work function change attributed to the thermal processing. Molybdenum is shown to be extremely sensitive with a work function change of -0.52 ± 0.04eV for Mo/SiO$_2$ and by -1.05 ± 0.12eV for Mo/Al$_2$O$_3$. The absolute work functions for the Mo/SiO$_2$ system are approaching the requirements of n- and p-MOSFET gate electrodes and there is evidence from the RBS measurements that there is a large process window for further optimisation.

1. Introduction

Future CMOS technologies are likely to require metal gate electrodes in order to eliminate poly-Si gate depletion, reduce gate resistance and improve matching behaviour. Conventional planar CMOS will require gate electrodes with two work-functions in order to achieve suitable Vt for both n- and p-MOSFETs. Currently, the required work functions (~4.25/5.25eV for n-/p-MOS) are achieved by doping of the poly-Si gate.

The integration issues associated with metal gates could be greatly eased if the electrode work-function at the dielectric interface could be adjusted after metal deposition. This would allow selective tuning of the threshold voltage and might even yield the two work functions required for CMOS without the need to remove one metal and redeposit a second. Several groups have reported a strong influence of nitrogen content at the metal-dielectric interface upon the work-function of TiN and Mo metal gates [1-3]. In those studies the nitrogen was introduced by low energy ion implantation. Unfortunately large implant doses are required in order to achieve a useful nitrogen concentrations at the lower interface and this can lead to gate reliability problems resulting from implant damage of the dielectric [3].

In this study the nitrogen was introduced by depositing a covering layer of over-stoichiometric TiN$_{1+x}$ and then diffusing the nitrogen to the lower interface with a rapid thermal anneal (RTA). This allows high concentrations of mobile nitrogen to be located close to the dielectric/metal interface prior to the diffusion anneal, and by a comparatively benign technique (in this case by sputtering). The effect is probably aided by the fact that mobile nitrogen is known to segregate to the dielectric/metal interface [4].

2. Experimental

The structures were fabricated on uniformly-doped p-type wafers (5-10Ωcm). All the metal layers were deposited in a single chamber; the Mo layers by DC sputtering; the Ta and TiN by RF sputtering. These were deposited on thermal oxides and on high-$\kappa$ dielectric layers with various thickness. The high-$\kappa$ dielectric layers were grown using an ASM POLYGON™ ALCVD (atomic-layer CVD) tool. Table 1 shows the full matrix of physical dielectric thickness and metal structure.

The metal stacks were then patterned into MOS capacitors by photolithography and etch. The pure Mo stacks were etched using NH$_4$OH/H$_2$O$_2$/H$_2$O (APM). The other stacks were dry etched using a CF$_4$/O$_2$ plasma.

Table 1. Nominal dielectric and metal electrode stack thickness for CV measurements

<table>
<thead>
<tr>
<th>$t_{\text{physical}}$=[6.5, 10, 15, 20, 25] (nm)</th>
<th>WF metal</th>
<th>Over-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>50nm Mo</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>10nm Mo</td>
<td>100nm TiN$_{1+x}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>50nm Mo</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>10nm Mo</td>
<td>100nm TiN$_{1+x}$</td>
</tr>
<tr>
<td></td>
<td>50nm Ta</td>
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<td>100nm TiN$_{1+x}$</td>
</tr>
</tbody>
</table>
chemistry. The TiN samples were subjected to an RTA (800°C for 30" in Ar), then given a passivating anneal (420°C/30’ in N₂/H₂). The other samples were given passivating anneals before and after the RTA. Capacitance-voltage (CV) measurements were also performed on these samples before and after RTA, in order to establish the influence of the thermal processing upon the work function of the metal. The CV measurements were performed using a Hewlet-Packard HP4285A LCR meter at measurement frequencies 1kHz-1MHz. The measured CV profiles were fitted using a model, described elsewhere [5], in order to extract the oxide capacitance (C_{ox}) and the flat-band voltage.

3. Materials characterisation

The nitrogen content of the TiN_{1+x} layers has been measured by RBS as x=0.1. In Fig. 1 the RBS spectra are plotted for two 10nm Ta/SiO₂ samples. One sample was covered with 100nm TiN_{1+x}, annealed (800°C/30” in Ar), and the TiN layer removed by wet etch. The RBS spectra reveal the presence of residual nitrogen only in the Ta layer which had the TiN cap. RBS spectra from samples after a range of anneal temperatures show that the residual nitrogen content in the Ta increases with temperature. This has been quantified using theoretical fits and the results are listed in Table 2. The highest value, following anneal at 1000°C, corresponds to a concentration of N in the Ta of ~35 at%.

4. Electrical characterisation

4.1 Molybdenum on SiO₂

CV curves for three Mo/SiO₂ structures are plotted in Fig. 2. Also shown are the fits to the data generated by the simulation. The best fits are obtained for the pure unannealed Mo sample. The same sample after RTA gives a similar flat-band voltage but there is some stretch-out of the profile indicative of interface states. There is a clear shift in the flat-band voltage (V_{FB}) for the TiN₁ₓ sample of −0.48±0.03V. Additional interface states are also apparent in the lower part of this CV profile but to a lesser extent than for the pure Mo post-RTA measurement.

If the effects of fixed charge upon the band bending are negligible then a simple extraction of the flat-band voltage can give a reliable estimate of the work function of the metal. However, this cannot be guaranteed, particularly in this case where the RTA after metal deposition was performed in a metal-compatible furnace not dedicated to front-end Si processing. The influence of fixed charge upon the measured flat-band voltage (V_{FB}) can be extracted by assuming that the fixed charge, Q_{int}, is located at the dielectric/Si interface. In this case the metal work function is given by,

\[ \phi_m = \phi_{Si} + qV_{FB} - \frac{Q_{int}}{C_{ox}}, \]  

where C_{ox} is the oxide capacitance and \( qV_{FB} = V_{FB} \), the flat-band voltage, is also known as the flat-band voltage of the Si substrate. If Q_{int} is independent of dielectric thickness, then \( \phi_{Si} \) can be extracted by extrapolating the measured flat-band voltage to \( t_{ox}=0 \) where the last term in Eq. 1 is negligible. This is shown in Fig. 3 for all the Mo/SiO₂ structures.

The fixed charge densities and electrode work functions extracted from the three plots are given in Table 3. The plots in Fig. 3 all exhibit a linear behaviour.
confirming the assumptions made in the derivation of Equation 1. The change in work function between the two post-RTA samples is \(-0.52 \pm 0.04\) eV. The effect of fixed charge is apparent from the finite gradient of all three plots with the pure Mo post-RTA samples having the highest fixed charge concentration. The values for the work functions given in Table 3 are very similar to those reported in the literature for nitrogen implantation studies in Mo/SiO\(_2\) MOS structures [3].

4.2 Molybdenum on Al\(_2\)O\(_3\)

CV curves for three Mo/Al\(_2\)O\(_3\) structures are plotted in Fig. 4 together with the fits generated by simulation. Again, the samples have a significantly larger interface state density after RTA and this is particularly noticeable for the TiN\(_{1+x}\) sample. This leads to a larger uncertainty in the values extracted for the flat-band voltage. The difference between the work functions for the post-RTA samples is \(-0.29 \pm 0.08\) V. It is of concern that the flat-band voltages for the pre- and post-RTA samples are so different (0.72V and 0.10V respectively). It is certainly conceivable that the work function is dependent upon thermal processing but this effect was not observed in the Mo/SiO\(_2\) sample set.

The origin of the discrepancy becomes clearer when all the flat-band voltages are plotted as a function of effective oxide thickness (EOT), as shown in Fig. 5. The sample without TiN has an extremely high fixed charge density after anneal (+1.5x10\(^{13}\) cm\(^{-2}\)) and this has dramatically affected the flat-band voltages, particularly for the thicker dielectrics. The work functions extracted for the pure Mo, pre- and post-RTA, are somewhat more consistent, as shown in Table 4, but are substantially larger than those seen for the Mo/SiO\(_2\) system or values in the literature [2,3]. The change in work function due to the TiN layer (-1.05±0.12eV) is also significantly larger than that observed for the Mo/SiO\(_2\) system. In contrast to these observations, replacing SiO\(_2\) with Al\(_2\)O\(_3\) is actually expected to decrease the metal work function [6].

<table>
<thead>
<tr>
<th>Sample set</th>
<th>(\phi_m) (eV)</th>
<th>Fixed charge (x10(^{13}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mo pre-RTA</td>
<td>4.987±0.013</td>
<td>+0.6±0.2</td>
</tr>
<tr>
<td>Pure Mo post-RTA</td>
<td>5.11±0.04</td>
<td>+3.6±0.5</td>
</tr>
<tr>
<td>Mo+TiN(_{1+x}) post-RTA</td>
<td>4.59±0.02</td>
<td>+2.0±0.5</td>
</tr>
</tbody>
</table>

Table 3. Parameters extracted from \(V_{FB}\) extrapolation for Mo/Al\(_2\)O\(_3\) samples

![Figure 3](image)

**Figure 3.** Flat-band voltage of the Mo/SiO\(_2\) samples as a function of SiO\(_2\) thickness

![Figure 4](image)

**Figure 4.** CV measurements and theoretical fits for Mo/Al\(_2\)O\(_3\) samples with \(t_{ox}=15\)nm (EOT=8nm)

![Figure 5](image)

**Figure 5.** Flat band voltage of the Mo/Al\(_2\)O\(_3\) samples as a function of EOT

<table>
<thead>
<tr>
<th>Sample set</th>
<th>(\phi_m) (eV)</th>
<th>Fixed charge (x10(^{13}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mo pre-RTA</td>
<td>5.53±0.01</td>
<td>-1.1±0.2</td>
</tr>
<tr>
<td>Pure Mo post-RTA</td>
<td>5.75±0.08</td>
<td>+14.5±1.5</td>
</tr>
<tr>
<td>Mo+TiN(_{1+x}) post-RTA</td>
<td>4.70±0.09</td>
<td>+0.3±1.7</td>
</tr>
</tbody>
</table>

Table 4. Parameters extracted from \(V_{FB}\) extrapolation for Mo/Al\(_2\)O\(_3\) samples
4.3 Tantalum on Al₂O₃

CV curves for three Ta/Al₂O₃ structures are plotted in Fig. 6 together with the fits generated by simulation. The EOT for these samples is 3.7nm. The flat-band voltages are plotted in Fig. 7 for all the Ta samples and the extracted parameters listed in Table 5.

From Fig. 7 it would seem that the thermal processing has as much influence upon the electrode work function as the presence of the TiN layer. The change in work function of the pure Ta sample during annealing is -0.08±0.02eV whereas the difference between the two annealed samples is -0.08±0.05eV. The CV curves for the samples with TiN all exhibit significant stretch-out, as seen for the TiN₁ₓ/Mo/Al₂O₃ samples. This suggests that nitrogen incorporation in the metal (Mo or Ta) is degrading the quality of these Al₂O₃ layers.

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5. Conclusions

The effects of nitrogen incorporation were studied for molybdenum on SiO₂ and on Al₂O₃ and for tantalum on Al₂O₃. RBS measurements have shown that substantial amounts of nitrogen can be diffused from a covering layer of over-stoichiometric TiN₁+x (x=0.1) into a 10nm Ta layer. It is also shown that this quantity of nitrogen increases with anneal temperature in the temperature range 500-1000°C. The work function of molybdenum is shown to be extremely sensitive to the presence of the TiN₁+x layer following anneal at 800°C for 30s. The work function changes by -0.52±0.04eV for a Mo/SiO₂ structure and by -1.05±0.12eV for a Mo/Al₂O₃ structure. The work function of Ta is less sensitive to the TiN covering layer, exhibiting a work function change of -0.08±0.02eV.

Solid state diffusion of nitrogen offers many advantages over nitrogen implantation as a means of adjusting gate work function, particularly in terms of gate dielectric quality. The results of CV measurements reported here suggest great potential for molybdenum as a candidate for a single-metal dual-work function approach to integrating metal gates into future CMOS technologies. The work functions are approaching the requirements of n- and p-MOS gate electrodes and RBS measurements of the diffused nitrogen indicate that there is a large process window for further optimisation of the nitrogen content and thus the work function.

6. References