Interfacial reaction in the sputter-deposited SiO\textsubscript{2}/Ti\textsubscript{0.1}W\textsubscript{0.9} antifuse system

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The effects of annealing temperature on the interfacial reactions and the antifuse I-V characteristics of ultra thin SiO\textsubscript{2} layer deposited on Ti\textsubscript{0.1}W\textsubscript{0.9} substrate were investigated. The interfacial reactions were analyzed using x-ray photoelectron spectroscopy and Auger electron spectroscopy with the sample which is in situ annealed under ultra high vacuum or ex situ annealed in a nitrogen atmosphere. The surface of the Ti\textsubscript{0.1}W\textsubscript{0.9} substrate was oxidized during sputter deposition of SiO\textsubscript{2} layer. Ti, W oxides consist of Ti\textsubscript{2}O\textsubscript{3} (Ti\textsubscript{2}O\textsubscript{5}), TiO\textsubscript{2}, WO\textsubscript{2}, and WO\textsubscript{3}. The WO\textsubscript{3} and Ti\textsubscript{2}O\textsubscript{3} decomposed into metallic W and Ti at 400 and 500 °C, respectively. The breakdown voltage of the antifuse decreased as the annealing temperature increased, due to the thinning of dielectric layer resulted from the decomposition of Ti, W oxides and the formation of metallic W and Ti. Annealing at 600 °C caused the reaction between metallic (Ti, W) and SiO\textsubscript{2} layer and formed elemental silicon in the dielectric layer, where SiO\textsubscript{2} layer completely lost its dielectric property. The breakdown of dielectric property might form a metallic channel in the SiO\textsubscript{2} film, which mainly contains metallic W, Ti, and Si.

I. INTRODUCTION

Metal/dielectric/metal structure is one of the most probable antifuse structures for field programmable gate arrays. This antifuse structure should have low leakage current in application to very large integrated circuit devices. For this reason, silicon oxide, silicon nitride, and amorphous silicon have been widely studied as an intermediate dielectric layer.\textsuperscript{1-4}

The dielectrics are usually deposited by sputtering technique, because the technique has several advantages such as good adhesion and uniform thickness over large planar area.\textsuperscript{5} Furthermore, low-temperature deposition is preferable to avoid the interaction with substrate material during the deposition. But for improved device characteristics, an annealing step after the low-temperature deposition is indispensable for recovery of the characteristics of dielectric material and improvement of the interfacial state.

In this article, we investigate the interfacial reactions between SiO\textsubscript{2} and Ti\textsubscript{0.1}W\textsubscript{0.9} in a SiO\textsubscript{2}/Ti\textsubscript{0.1}W\textsubscript{0.9} antifuse system before and after heat treatment by using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

Also, the breakdown characteristics of the SiO\textsubscript{2}/Ti\textsubscript{0.1}W\textsubscript{0.9} antifuse system with various annealing temperature are investigated and explained with the interaction between dielectric and metal.

II. EXPERIMENT

To investigate the effect of post anneal temperature to breakdown characteristics, layers of Ti\textsubscript{0.1}W\textsubscript{0.9} (500 nm thick) and SiO\textsubscript{2} (14 nm thick) were deposited successively on a chemically cleaned 5-35 Ω cm (100) p-type silicon wafer at room temperature. And the samples annealed at 400, 500, and 600 °C for 1 h in a nitrogen atmosphere. 400-nm-thick aluminum was deposited as an electrode. The breakdown behavior were explained with the interfacial reaction between dielectric and metal.

The antifuse structure of our interest consists of Al layer, 14-nm-thick SiO\textsubscript{2} layer, and 500-nm-thick Ti\textsubscript{0.1}W\textsubscript{0.9} layer on 5-35 Ω cm (100) p-type silicon wafer. Since the SiO\textsubscript{2} layer is deposited by a sputtering technique in an O\textsubscript{2} ambient, our interest focuses on the oxidation of the Ti\textsubscript{0.1}W\textsubscript{0.9} layer during sputter deposition of SiO\textsubscript{2} and on the interactions between SiO\textsubscript{2} layer and the Ti\textsubscript{0.1}W\textsubscript{0.9} layer during post annealing.

The interfacial reaction was analyzed by the monitoring of the bonding state of each element at the interface by using XPS of V. G. Scientific ESCALAB 200R and AES of MICROLAB 300D. For XPS analysis, Mg K\textsubscript{α} (1253.6 eV) radiation was used and the operating energy was 300 W. LaB\textsubscript{6} filament was operated at 10 kV for AES analysis and constant retard ratio for narrow scan analysis was 20. The thickness of SiO\textsubscript{2} film was measured with Philips CM20T/STEM transmission electron microscopy (TEM).

The sputtering using an argon ion etching gun is necessary to investigate the inner side of samples. In our samples, depth profile analysis should be done to investigate the interfacial reaction between dielectric and metal substrate. But sputtering using argon ion gun sometimes induces chemical modification of the sample. Reduction of oxidizing state due to break of the bonds between metal and oxygen by preferential sputtering may occur and the bonding states might be mixed.

The Ti\textsubscript{0.1}W\textsubscript{0.9} was oxidized at 750 °C for 1 h under oxygen atmosphere to check whether the sputtering using argon ion gun modified the chemical bonding states of the Ti, W oxides. Figure 1 shows the narrow XPS scan spectra of W (a)
FIG. 1. Montage profiles of W 4f (a) and Ti 2p (b) from the depth profile of Ti, W oxides.

and Ti (b) obtained during the depth profile analysis of the Ti, W oxides. After sputtering for 2 min, metallic tungsten appears and broadening of titanium peak is observed. This chemical modification due to sputtering damage was nearly saturated after sputtering for 4 min.

Because of the chemical modifications, 3-nm-thick SiO₂ layer, instead of 14-nm-thick SiO₂, was adopted to investigate the interfacial reactions between dielectric and metal using angle resolved XPS technique. SiO₂ (3 nm)/Ti₀.₇W₀.₃ (500 nm) sample was prepared for in situ annealing in XPS under ultrahigh vacuum (UHV; <1E⁻⁹ Torr). The sample was annealed from 100 to 700 °C for 1 h and cooled down to room temperature for XPS analyses. The angle resolved technique was applied for nondestructive depth profile analysis. In order to quantify the surface composition and identify the elemental bonding states, narrow scan spectra of all re-
TABLE I. Decompositions of W 4f, Ti 2p, Si 2p, and O 1s core level distributions.

<table>
<thead>
<tr>
<th>Peak attributions</th>
<th>Peak binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>% of area</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 4f</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W1 (TiW)</td>
<td>30.6</td>
<td>1.42</td>
<td>33</td>
</tr>
<tr>
<td>W2 (WO3)</td>
<td>32.8</td>
<td>1.61</td>
<td>19</td>
</tr>
<tr>
<td>W3 (WO3)</td>
<td>35.7</td>
<td>1.48</td>
<td>48</td>
</tr>
<tr>
<td>Ti 2p</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti1 (TiW)</td>
<td>453.9</td>
<td>1.88</td>
<td>18</td>
</tr>
<tr>
<td>Ti2 (Ti2O3,Ti3O5)</td>
<td>456.0</td>
<td>1.84</td>
<td>10</td>
</tr>
<tr>
<td>Ti3 (TiO3)</td>
<td>459.1</td>
<td>2.02</td>
<td>72</td>
</tr>
<tr>
<td>Si 2p</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si1 (Si)</td>
<td>99.0</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Si2 (SiO2)</td>
<td>103.5</td>
<td>1.92</td>
<td>100</td>
</tr>
<tr>
<td>O 1s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1 (O-Ti,W)</td>
<td>531.7</td>
<td>1.00</td>
<td>29</td>
</tr>
<tr>
<td>O2 (SiO2)</td>
<td>533.5</td>
<td>1.89</td>
<td>71</td>
</tr>
</tbody>
</table>

regions of interest were recorded with a pass energy of 20 eV and take-off angles of 10°, 50°, and 90°. Also, a 4-nm-thick SiO2 layer was deposited on a chemically cleaned silicon substrate in order to monitor the thermal stability of SiO2 itself under UHV.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the cross-sectional TEM image of an as-deposited SiO2 (3 nm)/Ti0.1W0.9 system. About 14-nm-thick gold layer was deposited on SiO2 layer to distinguish the SiO2 layer from epoxy, which was used for the cross-sectional TEM specimen preparation. The SiO2 layer was continuous and uniform. The interface was sharply defined and smooth.

Figure 3 shows the narrow XPS scan spectra of W (a), Ti (b), Si (c), and O (d) from the as-deposited SiO2 (3 nm)/Ti0.1W0.9 system with 10° take-off angle. The W 4f spectra in Fig. 3(a) resolved into three peak components as W1 (W in W-Ti), W2 (W-O in WO3), and W3 (W-O in WO5). The binding energy of 30.6 eV for W1 represents metallic W. This implies that no chemical shift is present when tungsten binds to titanium. The Ti 2p spectra in Fig. 3(b) also three peak components as Ti1 (Ti in Ti-W), Ti2 (Ti-O in Ti2O3, Ti3O5), and Ti3 (Ti-O in TiO3). The presence of TiO component can not be considered because Ti 2p3 in TiO shows the binding energy of 454.6 eV.6 The binding energy of 103.5 eV for Si2 (Si-O) peak in Fig. 3(c) implies that Si is completely oxidized state. Oxygen spectra in Fig. 3(d) presents O1 (O in Ti-W) and O2 (O in SiO2) bonding states. Peak attributions, binding energy, full width at half maximum, and percent of each peak area are listed in Table I.

The above XPS analysis indicates that the Ti0.1W0.9 substrate material is partially oxidized during the sputter deposition of SiO2 layer and the sputter-deposited SiO2 is in fully oxidized state. Note that the oxidation of substrate material forms WO2, W3, Ti2O3 (Ti3O5), and TiO2. Therefore, the SiO2/Ti0.1W0.9 system consists of SiO2, WO2, W3, Ti2O3 (Ti3O5), TiO2, and Ti0.1W0.9 phase.

The intensity variation of the peak components contributed to W and Ti of the as-deposited SiO2 (3 nm)/Ti0.1W0.9 system with take-off angles of 10°, 50°, and 90° is presented in Fig. 4. In this configuration, as the angle increases the
FIG. 6. Changes of bond distribution for SiO$_2$ (3 nm)/Ti$_{0.1}$W$_{0.9}$ system as a function of in situ annealing temperature with 10$^\circ$ of take-off angle; W1 (W-Ti), W2 (WO$_3$), W3 (WO$_3$), Ti1 (Ti-W), Ti2 (Ti$_2$O$_3$, Ti$_3$O$_5$), Ti3 (TiO$_2$), Si1 (Si), Si2 (SiO$_2$).

Contribution of surface bonding state to the observed peak intensity decreases. Therefore, the depth distribution of bonding states can be determined from comparison of the slope changes of various bonding contributions with take-off angle. Note that the metallic states of W and Ti were found under the oxidized state. This implies that W and Ti were partially oxidized at the interface during SiO$_2$ deposition.

Figure 5 shows the XPS spectra of W 4f (a), Ti 2p (b), Si 2p (c), and O 1s (d) in the SiO$_2$/Ti$_{0.1}$W$_{0.9}$ system, obtained at 10$^\circ$ take-off angle with various in situ annealing temperatures.

Figure 6 summarizes the intensity changes of bonding states for each element except oxygen. Slight increases for all bonding states were observed after annealing at 200 $^\circ$C. This is due to liberation of the physisorbed or chemisorbed oxygen on the surface. These relative intensities were maintained at 300 $^\circ$C but the decomposition of WO$_3$ began. Note that annealing above 300 $^\circ$C decomposes WO$_3$ (W3) and mainly forms metallic W (W1). The decomposition of WO$_3$ and formation of W result in the thinning of oxide thickness which might reduce dielectric breakdown voltage. Annealing at 400 $^\circ$C clearly reduces WO$_3$ and increases metallic W. Also, note that WO$_2$ (W2) and Ti$_2$O$_3$, Ti$_3$O$_5$ (Ti2) were slightly increased. After annealing at 500 $^\circ$C sharp increase of metallic W and Ti, sharp decrease of WO$_3$, and slight decrease of WO$_2$ and TiO$_2$ were found. Note that elemental Ti forms by the decomposition of TiO$_2$. The Ti, W-oxides layer is further thinned by the decomposition. Above 600 $^\circ$C, sharp decrease of SiO$_2$ (Si2) and sharp increase of elemental Si (Si1) were observed in addition to the increase of metallic W and Ti. The Si 2p peak at 99.0 eV of binding energy appears due to the decomposition of SiO$_2$. The metallic W, Ti, and Si in-
crease and SiO₂ decreases above 600 °C, but the other bonding states were almost constant.

Through angle resolved analysis, this elemental silicon was revealed to be found mainly below the SiO₂ layer. The silicon may bind with W and Ti, and form silicides because metallic silicides are easily formed by annealing above 500 °C. By XPS analysis, we can not distinguish elemental silicon from silicon in silicide, because they have almost the same binding energy of about 99.0 eV. Since the SiO₂ decomposed and elemental Si appeared in a SiO₂/Ti₀.₁W₀.₉ system at 600 °C, thermal stability of pure SiO₂ was analyzed through in situ annealing in XPS and the bonding change was examined to confirm.

Figure 7 shows composition change of bonding states in SiO₂ (4 nm)/Si system as a function of in situ annealing temperature. Composition of oxygen slightly decreases but maintains almost constant up to 700 °C. From this result, it can be said that silicon oxide itself is thermally stable under UHV up to 700 °C. Also this result suggests that the decomposition of SiO₂ is induced by the reaction with metallic W and Ti, resulting in the formation of Ti, W silicides at 600 °C.

Figure 8 shows the scanning electron micrographs of the surfaces of the as deposited and 600 °C-annealed SiO₂ (14 nm)/Ti₀.₁W₀.₉ system. The sample annealed at 600 °C, white specks were found all over the surface. While no speck was found on the surface of the as deposited sample. We did not find a speck on the samples annealed up to 500 °C. AES point analyses on the spots showed the existence of Si, Ti, W, and O. Narrow scan spectra of Ti and W Auger peaks showed that they are metallic states. And with KLL Auger spectrum of Si, we found that there are two peaks (Fig. 9), which can be identified as two chemical states of silicon. Therefore, two kinds of control samples as elemental Si and oxidized Si are prepared and analyzed. Actually, the oxidized and elemental Si originate from the SiO₂ layer above the white specks, discussed in the previous paragraph with the angle resolved analysis. Therefore, it can be said that the white specks are Ti, W silicides, although the exact structure should be further studied by TEM, which is beyond the scope of this article.

Figure 10 represents I-V characteristics of an Al (400 nm)/SiO₂ (14 nm)/Ti₀.₁W₀.₉ (500 nm) antifuse system as a function of annealing temperature. The breakdown voltage of the system is 10.2 V before annealing. And breakdown voltage decreases as the annealing temperature increases. The breakdown voltage of the device annealed at 400 and 500 °C are 7.2 and 4.3 V, respectively. Note that the system annealed above 600 °C failed to show the characteristics of the dielectric film. From our previous interface analysis, it is possible to explain the I-V characteristics shown in Fig. 10. The breakdown voltage of the as-deposited system is high because the SiO₂ layer and the Ti, W-oxides layer formed during the sputter deposition of SiO₂ layer. The breakdown voltage reduced to 7.2 V at 400 °C, at which WO₃ in Ti, W oxides on Ti₀.₁W₀.₉ substrate decomposed to form metallic W and WO₂. The formation of metallic W might degrade the dielectric properties of Ti, W-oxide layers. Further decrease of breakdown voltage observed at 500 °C, where metallic Ti also formed in addition to further formation metallic W. It is likely that the formation of metals induces rougher SiO₂/Ti₀.₁W₀.₉ interface.

The antifuse sample annealed at 600 °C completely loses its antifusing characteristic. Note that the SiO₂ dielectric layer decomposes at this temperature forms elemental Si, which might form an electrical path between metal electrodes. The elemental Si may exist as Ti, W silicides and appears in white specks as SEM photograph (Fig. 8). Since pure SiO₂ is thermally stable even at 700 °C, the interfacial reaction between SiO₂ and metallic Ti, W plays a key role in the failure of antifuse device characteristics.

IV. CONCLUSIONS

Interface analysis between SiO₂ (3 nm) and Ti₀.₁W₀.₉ (500 nm) layers showed the following results. Sputter deposition of SiO₂ at room temperature formed Ti, W-oxide phases on the Ti₀.₁W₀.₉ surface. The existing Ti, W-oxide phases were TiO₂, Ti₂O₃ (Ti₃O₅), WO₂, and WO₃. The in


**situ** annealing of the sample in XPS under UHV condition revealed that WO₃ and TiO₂ began to decompose into metallic W and Ti at 400 and 500 °C, respectively. Also, the amount of WO₂ and TiO₂ increased slightly. The reduction of metallic oxides might induce the thinning of dielectric and the roughening of interface, resulted in the decrease of breakdown voltage in the antifuse structure. Moreover, the metallic W and Ti reacted with SiO₂ and partially reduced SiO₂ into elemental Si at 600 °C, where SiO₂ itself is thermally stable. The metallic phases existed as white specks on all over the sample surface and might form metal channel in the SiO₂ dielectric film, resulted in losing dielectric property at 600 °C. TEM analysis for the structure and morphology of the metal channel could be useful for the further understanding of microstructure-property relationship.