Hydrogen Ion Sensing Properties of Niobium Oxide by RTA and Thickness effect

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1. Introduction
High dielectric constant high-k materials including Al2O3 [1], Ta2O5 [2], and HfO2 [3] have been studied to replace Si3N4 [4] membrane for ion sensitive field-effect-transistors (ISFET) application due to the better stability and sensitivity. Additional advantage of high-k materials is the process compatibility for future technologies, such as the candidate for gate dielectric in CMOS and capacitance dielectric in DRAM and RF application. In this study, niobium oxide (NbOx) which is a well-implemented capacitance dielectric in DRAM and RF application. In this study, niobium oxide (NbOx) which is a well-implemented capacitance dielectric in DRAM and RF application.

2. Experimental
Single-layer Electrolyte-insulator-semiconductor (EIS) structures were fabricated to investigate hydrogen ion sensing properties. [5] NbOx layer was deposited by radio frequency rf sputtering directly on p-type (100) silicon wafer after standard RCA cleaning. The Nb target with 99.9% purity was used in reactive rf sputtering with the power of 300 W. The flow rate of Ar and O2 was 20 and 5 sccm, respectively. The thickness of NbOx sensing membrane was controlled by deposition time and then verified by ellipsometer measurement. Then, the PDA was performed in N2 and O2 ambient at temperature of 500, 700, and 900°C for 1 min, respectively. Detailed process flows of all groups are shown in Fig. 1. pH sensitivities of sensing membranes were all extracted by capacitance-voltage (C-V) curves of EIS structures measured in various pH buffer solution of Merck Inc. through Ag/AgCl reference electrode by HP4284A high precision LCR meter.

3. Results and Discussion
C-V curves were measured in various standard pH buffer solutions to collect the pH-dependent C-V shift as shown in Fig. 2. pH sensitivity can be calculated by the linear fitting between the output voltage and pH value. Linearity of the fitting curve can be an index for real application in wide pH range. Totally 14 groups designed with 3 different factors including NbOx thickness (5 and 30nm), PDA ambient (N2 and O2), and PDA temperature (500, 700, and 900°C), respectively. In Fig. 3, the sensitivity and linearity of the group with 5nm-thick NbOx with PDA in N2 ambient at different temperature are presented. Low linearity which is less than 99% refers to poor response may from some minor surface damages by insufficient densification. In Fig. 4, 5nm-thick NbOx with PDA in O2 ambient at different temperature shows higher linearity in the group with PDA at 500 and 700°C than the group without PDA and with PDA at 900°C. In Fig. 5 and Fig. 6, very similar temperature dependent behavior of pH sensitivity and linearity can be observed both in N2 and O2 ambient. Linearity and pH sensitivity can be improved by the application of PDA at temperature from 500 to 700°C. With the PDA temperature at 900°C, sensitivity and linearity are slightly reduced. As shown in Fig. 7, morphology check is performed by C-AFM analysis. NbOx or other dielectrics start to crystalize with PDA at temperature from 500 to 700°C, which makes changes from amorphous type to poly-crystal type. In the meantime, surface roughness is increased by larger grain size and following larger surface area per unit square. Then pH sensitivity can be increased by more surface site density. [6] However, the grain boundaries could lead to more leakage path to makes worse stability including drift and hysteresis effect. As listed in Table 1, all pH sensing performance including drift and hysteresis can be easily compared. 5nm-thick NbOx needs PDA in O2 ambient to increase pH sensitivity by additional oxidation. In 30nm-thick NbOx, drift and hysteresis can be reduced by PDA in O2 ambient than in N2 ambient. The optimization in this study is 30nm-thick NbOx with PDA between 500 and 700°C in O2 ambient.

4. Conclusions
Niobium oxide is firstly investigated as a pH sensing membrane in single-layer EIS structure. To have higher pH sensitivity and linearity, PDA is suggested to perform at 500 to 700°C in O2 ambient for 30nm-thick EIS structure in real application.

Acknowledgements
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References
Fig. 1 Process flow of NbOx-EIS structures with (a) thickness, (b) PDA in N₂ and (c) PDA in O₂.

Fig. 2 C-V curves measured in various pH buffer solutions of 30nm-thick NbOx-EIS structure with PDA in N₂ ambient at 700°C.

Fig. 3 pH sensitivity and linearity of 5nm-thick NbOx-EIS structure with PDA in N₂ ambient at various temperatures.

Fig. 4 pH sensitivity and linearity of 5nm-thick NbOx-EIS structure with PDA in O₂ ambient at various temperatures.

Fig. 5 pH sensitivity and linearity of 30nm-thick NbOx-EIS structure with PDA in N₂ ambient at various temperatures.

Fig. 6 pH sensitivity and linearity of 30nm-thick NbOx-EIS structure with PDA in O₂ ambient at various temperatures.

Table 1 Comparison on pH sensing properties of NbOx-EIS structure by all experimental groups.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>PDA ambient</th>
<th>Temp. (°C)</th>
<th>Sensitivity (mV/pH)</th>
<th>Linearity (%)</th>
<th>Drift (mV/h)</th>
<th>Hysteresis (mV)</th>
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<tr>
<td>5</td>
<td>w/o</td>
<td>0</td>
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<td>98.46</td>
<td>-3.1</td>
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<td>500</td>
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<td>95.76</td>
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<td>10.8</td>
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<td></td>
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<td>700</td>
<td>58.3</td>
<td>98.91</td>
<td>-1.9</td>
<td>5.8</td>
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<tr>
<td></td>
<td></td>
<td>900</td>
<td>38.1</td>
<td>96.92</td>
<td>-1.7</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>500</td>
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<td>99.76</td>
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<tr>
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<tr>
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<td>53.5</td>
<td>99.95</td>
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<td>58.5</td>
<td>99.49</td>
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</tr>
</tbody>
</table>

Fig. 7 AFM analysis on 30nm-thick NbOx with PDA in N₂ ambient at (a) 0, (b) 500, (c) 700, (d) 900°C.