Self-cleaning Effects on Atomic Layer Deposition (ALD) of Al₂O₃ on InGaAs with Several Surface Treatments

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1. Introduction

III-V compounds are one of the best candidates as channel materials for future CMOS technology [1]. The success of 22nm generation devices will also require integration of III-V compounds with high-k dielectric [2]. However, the lack of high quality high-k/III-V interface that hinder the performance of devices remain a big challenge. In this work, we studied in details the role of trimethyl aluminum (TMA) in interfacial self-cleaning effect during ALD of Al₂O₃ on n-In₀.7Ga₀.3As epilayer. Good electrical characteristics of the MOS devices confirm the self-cleaning and surface treatments effects.

2. Experimental

The substrates employed for this study were n-In₀.7Ga₀.3As/In₀.53Ga₀.47As structure grown by molecular beam epitaxial (MBE) on n-InP wafers. Several starting surfaces were prepared before employing in-situ half ALD cycles TMA pretreatments (list in table 1).

<table>
<thead>
<tr>
<th>Sam.</th>
<th>Surface treatment process</th>
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</thead>
<tbody>
<tr>
<td>i</td>
<td>Bare native oxide covered (w/o treatment and oxide dep.)</td>
</tr>
<tr>
<td>ii</td>
<td>Native oxide covered → 1 half ALD cycle TMA</td>
</tr>
<tr>
<td>iii</td>
<td>Native oxide covered → 5 half ALD cycles TMA</td>
</tr>
<tr>
<td>iv</td>
<td>Native oxide covered → 10 half ALD cycles TMA</td>
</tr>
<tr>
<td>v</td>
<td>HCl:H₂O = 1:10, 1min → 10 half ALD cycles TMA</td>
</tr>
<tr>
<td>vi</td>
<td>HCl:H₂O = 1:10, 1min; (NH₄)₂S, 20min → 10 half ALD cycles TMA</td>
</tr>
</tbody>
</table>

Tab. 1. Samples with different treated conditions

3. Results and discussion

Fig.1 illustrates the XPS analysis on As 3d and In 3d₅/₂ spectra of samples (i), (ii), (iii) and (iv). The reduction of native oxides was achieved after employing several half ALD cycles of TMA as shown in samples (ii), (iii) and (iv). This indicates that TMA plays an important role in removing the native oxides through self-cleaning by ligand exchange reaction between it and native oxides. As can be seen in As 3d spectra, the reduction of As₂O₅ oxide corresponding to As⁺⁵ oxidation state is not obvious. In contrast, the reduction of As₂O₃ oxide corresponding to As⁺³ is significant. This demonstrates that the reaction between TMA and native oxides is a selective reaction. The referred reaction between As₂O₃ and TMA can be explained by considering As (in As₂O₃) and Al (in TMA-(CH₃)₃Al) both are in the same oxidation state of 3⁺. Similarly, the reduction of In-related oxides is also mostly occurred from the reaction between In₂O₃ and TMA.

After that ~2nm and ~10nm Al₂O₃ were deposited at 200°C for XPS and MOS electrical characteristics measurements, respectively. MOS devices were fabricated by carrying out postdeposition annealing (PDA) in N₂ at 500°C for 30s. After that Ti/Pt/Au gate metal and Au/Ge/Ni/Au backside metal were formed and followed by post metal annealing (PMA) in N₂ at 400°C for 30s.
Fig. 1. As3d and In3d5/2 XPS spectra of samples (i), (ii), (iii) and (iv). As show in fig.1, there is almost no change in the spectrum for samples with 1, 5 and 10 cycles of TMA pretreatments. This reveals that most of the ligand exchange reactions between TMA and native oxides occurred and stopped right after the first cycle of TMA. This suggests that after first TMA pulse, the reaction between it and the native oxides formed a complete Al$_2$O$_3$ layer on the top. TMA will no longer be able to react with native oxides beneath the Al$_2$O$_3$ layer.

Fig. 2. As3d and In3d5/2 spectra of sample (iv), (v) and (vi)

Fig. 2 shows the As3d and In3d5/2 spectra of samples (iv), (v) and (vi). After employing surface treatment and TMA pretreatment, no As-O bonding was detected by XPS, In-O bonding was also decreased significantly. This indicates that while native oxides were not complete removed by self-cleaning effect, the combination of surface treatment and TMA pretreatment was necessary.

Fig. 3. C-V curves of samples (iv), (v) and (vi) with 10nm Al$_2$O$_3$

The C-V loops for capacitor of sample (iv), (v) and (vi), respectively are shown in fig.3. The effects of self-cleaning and surface treatment result in low frequency dispersion (3.45% ÷ 3.8% between 1kHz and 100kHz); low hysteresis at flat band condition (80÷100mV). The leakage current density is smaller than 10^{-4}A/cm$^2$ for all samples within ±2.5V. The mid-band gap $D_n$ estimated by conductance method were about 2.3x10^{12}, 1.5x10^{12} and 8x10^{11} eV$^{-1}$cm$^{-2}$ for samples (iv), (v) and (vi), respectively. Lower $D_n$ was achieved on samples with surface treatments before TMA pretreatment.

**Conclusion**

In conclusion, we have demonstrated that the reduction of native oxides by TMA was mostly effective and stop right after the first pulse. The further removed of native oxide can be achieved with both surface treatment and TMA pretreatment. Good result in MOS devices was observed on the samples prepare with these treatments.

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**References**
