Plasma Enhanced Liquid Source-CVD and Rapid Thermal Annealing of Tantalum Penta Oxide Dielectric Material

P. A. Murawala, M. Sawai, T. Tatsuta and O. Tsuji
Research & Development Center, Samco International Incorporated, 33, Tanakamiya-Cho, Takeda, Fushimi-ku, Kyoto 612, Japan
and
Sz. Fujita and Sg. Fujita
Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan

Tantalum penta oxide (Ta₂O₅) insulator material has been deposited from a penta ethoxy tantalum [Ta(OC₂H₅)₅] liquid source by PECVD. Au/Ta₂O₅/n+p-Si MOS diodes exhibited very well defined C-V characteristics with flat band voltages as low as about 0.1V, low leakage currents, high breakdown voltages and high dielectric constant (ε=25). Rapid thermal annealing (RTA) performed for the first time on Ta₂O₅, at 700°C and 900°C for 5 minutes showed much improved electrical properties. All results suggest growth of high quality Ta₂O₅ films from a carbon-based Ta liquid source, due to an effect of plasma enhanced deposition process.

1. INTRODUCTION

Tantalum penta oxide (Ta₂O₅) has received much attention in I.C. technology for its application as storage capacitors and as gate insulators in DRAM MOS devices due to its high dielectric constant.

Recently, many efforts have been made to deposit Ta₂O₅ using different source materials and deposition techniques. For the source material of Ta in CVD, despite the good controllability of flow rate over a wide range using liquid sources, solid sources such as TaCl₅ are widely applied in order to minimize the carbon contamination from liquid sources. In practice, poor electrical properties of Ta₂O₅ deposited using liquid sources by thermal CVD or photo CVD have been attributed to carbon contamination. However, we consider that plasma CVD using liquid sources, which has been little investigated, is more effective to decompose the carbon-related bonds in source materials and contribute to lower carbon contamination, resulting in better electrical properties.

In past, post deposition annealing has been considered to be desirable for further improvements of electrical properties; for this purpose ozone-related annealing techniques has been developed. However, rapid thermal annealing (RTA) can more easily and practically be performed over large wafers.

In the present work, we have deposited Ta₂O₅ by plasma enhanced liquid-source chemical vapor deposition (LS-CVD) using Ta(OC₂H₅)₅ source and have investigated basic deposition conditions, electrical properties and effects of RTA.

2. PLASMA ENHANCED LS-CVD OF Ta₂O₅

Deposition of Ta₂O₅ was carried out in Samco's model PD240 by using plasma enhanced LS-CVD technique (Fig. 1).

![Fig.1 Experimental set-up for plasma enhanced liquid source-CVD (SAMCO model PD240).](image)

Table 1 shows the typical deposition conditions. Source material Ta(OC₂H₅)₅ is liquid at room temperature, its melting point (M.P.) is 21°C, boiling point (B.P.) is 146°C and vapor-pressure at 140°C is 0.1 mm Hg.

<table>
<thead>
<tr>
<th>Source</th>
<th>- Ta(OC₂H₅)₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank Temperature</td>
<td>160-180°C</td>
</tr>
<tr>
<td>Line Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>475°C</td>
</tr>
<tr>
<td>Carrier gas - N₂</td>
<td>50 SCCM</td>
</tr>
<tr>
<td>Reactive gas - O₂</td>
<td>50 SCCM</td>
</tr>
<tr>
<td>RF Power Density</td>
<td>0.38 W/cm²</td>
</tr>
</tbody>
</table>

Table 1: Typical deposition conditions
A comparative study of the reported deposition rates of Ta$_2$O$_5$ by different technique and material is demonstrated in the Table 2. Saitoh$^5$ has reported $R_d=45$ $\Omega$/min., by LPCVD using Ta(OCH$_3$)$_5$ but their substrate temperature is too high for use in device application. At such high temperatures device property may degrade due to possible interdiffusion. Yamagishi$^2$ have achieved $R_d=70$ $\Omega$/min. by photo-CVD using Ta(OCH$_3$)$_5$, however by thermal CVD they got only $R_d=20$ $\Omega$/min. Matsui$^1$ have reported $R_d=32 \Omega$ by photo-CVD using TaCl$_5$, Teravainenhorn$^6$ reported $R_d=16$ $\Omega$/min. by D.C. sputtering (Ta target).

Table 2. : Deposition rates

<table>
<thead>
<tr>
<th>Deposition Technique</th>
<th>$T_s$ (°C)</th>
<th>$R_d$ (Ω/min.)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPCVD [Ta(OCH$_3$)$_5$]</td>
<td>700</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>Photo CVD [Ta(OCH$_3$)$_5$]</td>
<td>-</td>
<td>70 (20)</td>
<td>2</td>
</tr>
<tr>
<td>Photo CVD (TaCl$_5$)</td>
<td>450</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>D.C. Sputtering (Ta Target)</td>
<td>-</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>ECR-CVD (TaCl$_5$)</td>
<td>200</td>
<td>400</td>
<td>7</td>
</tr>
<tr>
<td>PE-LSCVD [Ta(OCH$_3$)$_5$]</td>
<td>475</td>
<td>64</td>
<td>*</td>
</tr>
</tbody>
</table>

In comparison to above reported data, our $R_d=64$ $\Omega$/min. by PE-LSCVD is much better and we hope that it will enhance by the use of photo-irradiation and/or UV-O$_3$ techniques. Of course, $R_d=400$ $\Omega$/min obtain by ECR is an exempt of a much faster rate$^7$.

3. ELECTRICAL PROPERTIES

3.1 CAPACITANCE-VOLTAGE CHARACTERISTICS

Figure 2(a,b) shows 1 MHz C-V characteristics of Au-Ta$_2$O$_5$/n,p-Si MOS diodes (ohmic contact: AuSb for n-Si, AuGe for p-Si, top electrode: Au-1mmO, Si:1$\times$10$^{18}$ cm$^{-3}$). Very well defined C-V characteristics together with strong accumulation effect were obtained on as-grown Ta$_2$O$_5$. The flat band voltage (Vfb) is as low as about -0.1V in both cases. Higher values of dielectric constant (ε=25) were obtained on n$^+$ Si(8$\times$10$^{18}$ cm$^{-3}$). Tanimoto$^8$ also reported C-V curve for Al/Ta$_2$O$_5$/Si MOS structure where Ta$_2$O$_5$ was grown by photo-CVD using ozone by using TaCl$_5$ solid source. Although they did obtain typical C-V characteristic, but its Vfb is much shifted towards positive bias indicating some charge exists in Ta$_2$O$_5$ film. It is important that we by using PE-LSCVD of Ta(OCH$_3$)$_5$ could achieve much better C-V curve with negligible Vfb values.

3.2. CURRENT-VOLTAGE CHARACTERISTICS

Figure 3 is the current voltage characteristics of Au-Ta$_2$O$_5$/Si MOS diode. Current, as low as about 6 x 10$^{-8}$A/cm$^2$ could be achieved for 1 MV/cm electric field and breakdown occurs at 5 MV/cm. We have for the purpose of comparison, also plotted I-V data obtained from literature for carbon-based liquid source materials by different deposition techniques. Numasawa$^9$ reported I-V data from Ta(OCH$_3$)$_5$ by LPCVD and then they used TaCl$_5$ to have better electrical properties. Shinriki$^3$ performed two-step annealing technique to reduce leakage currents of Ta$_2$O$_5$ film grown from Ta(OCH$_3$)$_5$ by LPCVD. They also performed UV-O$_3$ annealing at 300°C. They could achieve better I-V characteristics only after two step annealing [UV-O$_3$ + dry O$_2$ at 800°C]. Yamagishi$^2$ reported photo-CVD of Ta$_2$O$_5$ from Ta(OCH$_3$)$_5$ liquid source.

From this comparison of I-V data it is evident that leakage currents are two orders of magnitude smaller, obtained by us by using plasma enhanced LSCVD, then those obtained by LPCVD.

In the chemical analysis, carbon concentration of our Ta$_2$O$_5$ film was below the detectable limit in AES measurements$^{10}$. 

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Fig. 2: Well defined capacitance voltage characteristics of Au/Ta$_2$O$_5$/Si MOS diodes.
In plasma CVD, chemical reactions result from electron-impact dissociation of precursor gases in the plasma glow discharge. As the rf power intensity increases, number of ions also increases which enhances plasma ion bombardment and results in dissociation of precursors. Therefore in PECVD, Ta(O₂H₅)₅ will be effectively decomposed and will result in nearly carbon-free Ta₂O₅ films.

4. RAPID THERMAL ANNEALING (RTA)

RTA was performed for the first time in (RTA equipment of AST, Germany) N₂ atmosphere for 5min. at 700°C and 900°C. In Fig. 4 we show effects of annealing on resistivity of the film. In as-grown sample resistivity is 10¹² Ω-Cm, which improves to 10¹⁴ - 10¹⁵ Ω-Cm for 1MV/cm applied fields as an effects of rapid thermal annealing. These resistivity values are indicative of high quality insulator. Also breakdown do not occur even up to investigated 10 MV/cm applied electric field in annealed samples.

Annealing results suggest that defects and impurities present in Ta₂O₅ out-diffuses, resulting in improved film quality. Specially as an effect of rapid annealing the whole Ta₂O₅ film faces a rapid lattice vibration, rearranging its stoichiometry structure (Ta₂O₅), out diffusing impurities and improving the crystal defects.

5. CONCLUSION

In conclusion, we have succeeded in growing high quality Ta₂O₅ dielectric material from a carbon based liquid source Ta(O₂H₅)₅ by using plasma enhanced CVD technique. Our as grown Ta₂O₅ shows very well defined C-V characteristics with Vfb as low as about 0.1eV for both n-p-Si, dielectric constant greater than 25 and much low leakage current as compared to those reported earlier by other CVD techniques for carbon based source material. RTA further improves films quality. Hence plasma enhanced LSCVD grown film can be more suitable in I.C. technology.

6. REFERENCES

4) TRI Chemical Laboratory Inc., Japan.