Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 527-529 A-4-3

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 (Ta_2O_5) insulator material has been deposited from a penta ethoxy tantalum [$Ta(OC_2H_5)_5$] liquid source by PECVD. Au/Ta_2O_5/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 (>25). Rapid thermal annealing (RTA) performed for the first time on Ta_2O_5, at 700°C and 900°C for 5 minutes showed much improved electrical properties. All results suggest growth of high quality Ta_2O_5 films from a carbon-based Ta liquid source, due to an effect of plasma enhanced deposition process.

1. INTRODUCTION

Tantalum penla oxide (Ta_2O_5) 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 Ta_2O_5 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 $TaCl_5$ are widely applied in order to minimize the carbon contamination from liquid sources[1]. In practice, poor electrical properties of Ta_2O_5 deposited using liquid sources by thermal CVD or photo CVD has been attributed to carbon contamination[2]. 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[3]. However, rapid thermal annealing (RTA) can more easily and practically be performed over large wafers.

In the present work, we have deposited Ta_2O_5 by plasma enhanced liquid-source chemical vapor deposition (LS-CVD) using $Ta(OC_2H_5)_5$ source and have investigated basic deposition conditions, electrical properties and effects of RTA.

2. PLASMA ENHANCED LS-CVD Of Ta_2O_5

Deposition of Ta_2O_5 was carried out in Samco's model PD240 by using plasma enhanced LS-CVD technique (Fig. 1).

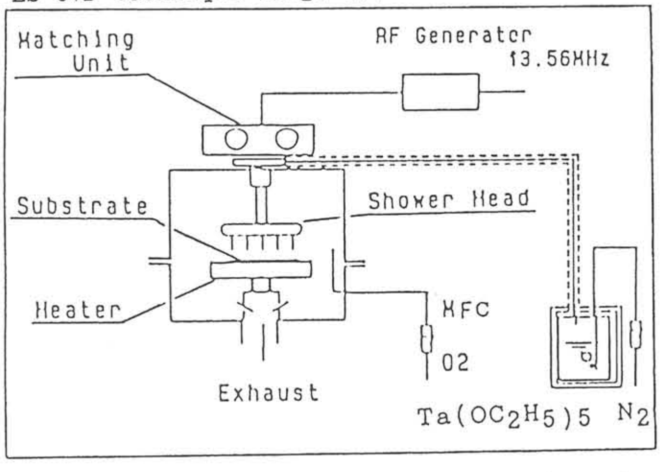

Fig.1 Experimental set-up for plasma enhansed liquid source-CVD (SAMCO model PD240).

Table 1 shows the typical deposition conditions. Source material $Ta(OC_2H_5)_5$ is liquid at room temperature, its melting print (M.P.) is 21°C, boiling point (B.P.) is 146°C and vapor-pressure at 140°C is 0.1 mm Hg[4].

Table 1. : Typical deposition conditions

Source	- $Ta(OC_2H_5)_5$
Tank Temperature	- 160-180°C
Line Temperature	- 180°C
Substrate Temperture	- 475°C
Carrier gas - N_2	- 50 SCCM
Reactive gas - O_2	- 50 SCCM
RF Power Density	- 0.38 W/cm^2

A comparitive study of the reported deposition rates of Ta_2O_5 by different technique and material is demonstrated in the Table 2. Saitoh[5] has reported Rd=45 Å/min., by LPCVD using $Ta(OC_2H_5)_5$ 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 Rd=70 Å/min. by photo-CVD using $Ta(OCH_3)_5$, however by thermal CVD they got only Rd=20 Å/min. Matsui[1] have reported Rd=32Å by photo-CVD using $TaCl_5$, Teravaninthorn[6] reported Rd=16 Å/min. by D.C. sputtering (Ta target).

Table 2. : Deposition rates

Deposition Technique	Ts (°C)	Rd (Å/min.)	Ref
LPCVD [$Ta(OC_2H_5)_5$]	700	45	5
Photo CVD [$Ta(OCH_3)_5$]	-	70 (20)	2
Photo CVD ($TaCl_5$)	450	32	1
D.C.Sputtering (Ta Target)	-	16	6
ECR-CVD ($TaCl_5$)	200	400	7
PE-LSCVD [$Ta(OC_2H_5)_5$]	475	64	*

* Present work.

In comparision to above reported data, our Rd=64 Å/min. by PE-LSCVD is much better and we hope that it will enhance by the use of photo-irradiation and/or $UV\text{-}O_3$ techniques. Of course, Rd=400 Å/min obtaind 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_2O_5/n,p-Si MOS diodes (ohmic contact: AuSb for n-Si, AuGa for p-Si, top electrode: Au-1mmO, Si:$1*10^{15}cm^{-3}$). Very well defined C-V characteristics together with strong accumulation effect were obtained on as-grown Ta_2O_5. The flat bond voltage (Vfb) is as low as about -0.1V in both cases. Higher values of dielectric constant (>25) were obtained on n^+ Si($8*10^{18}$ cm^{-3}). Tanimoto[8] also reported C-V curve for $Al/Ta_2O_5/Si$ MOS structure where Ta_2O_5 was grown by photo-CVD using ozone by using $TaCl_5$ solid source. Although they did obtain typical C-V characteristic, but its V_{fb} is much shifted towards positive bias indicating some charge exists in Ta_2O_5 film. It is important that we by using PE-LSCVD of $Ta(OC_2H_5)$ could achieve much better C-V curve with negligible Vfb values.

3.2. CURRENT-VOLTAGE CHARACTERISTICS

Figure 3 is the current voltage characteristics of $Au/Ta_2O_5/Si$ MOS diode. Current, as low as about $6 \times 10^{-8}A/cm^2$ could be achieved for 1 MV/cm electric field and

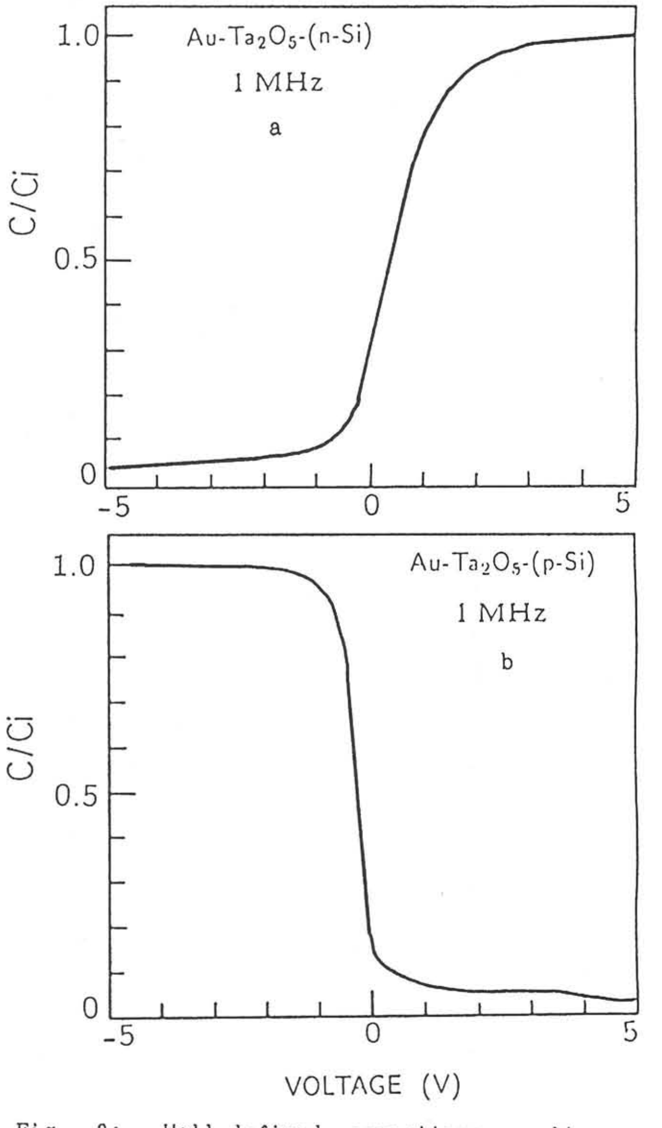

Fig. 2: Well defined capacitance voltage characteristics of $Au/Ta_2O_5/Si$ MOS diodes.

breakdown occurs at 5 MV/cm. We have for the purpose of comparision, 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 $Ta(OC_2H_5)_5$ 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_2O_5 film grown from $Ta(OC_2H_5)_5$ by LPCVD. They also performed $UV\text{-}O_3$ annealing at 300°C. They could achieve better I-V characteristics only after two step annealing [$UV\text{-}O_3$ + dry O_2 at 800°C]. Yamagishi[2] reported photo-CVD of Ta_2O_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_2O_5 film was below the detectable limit in AES measurements[10].

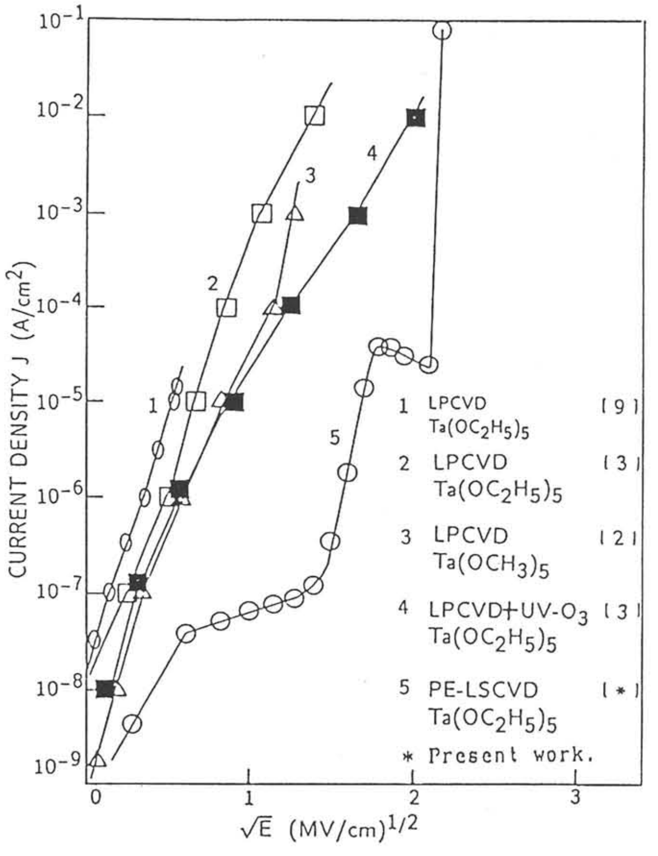

Fig. 3: Current voltage characteristics of Ta_2O_5. Our data is compared with those reported for carbon-based liquid sources.

In plasma CVD, chemical reactions results from electron-impact dissociation of precursor gases in the plasma glow discharge. As the rf power intensity increases, number of ions also increases which exhances plasma ion bombardment and results in dissociation of precursors. Therefore in PECVD, $Ta(OC_2H_5)_5$ will be effectively decomposed and will result in nearly carbon-free Ta_2O_5 films.

4. RAPID THERMAL ANNEALING (RTA)

RTA was performed for the first time in (RTA equipment of AST, Germany) N_2 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 10^{13} Ω-Cm, which improves to 10^{14} - 10^{15} 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 Ta_2O_5 out-diffuses, resulting in improved film quality. Specially as an effect of rapid annealing the whole Ta_2O_5 film faces a rapid lattice vibration, rearranging its stoichiometry structure (Ta_2O_5), out diffusing impurities and improving the crystal defects.

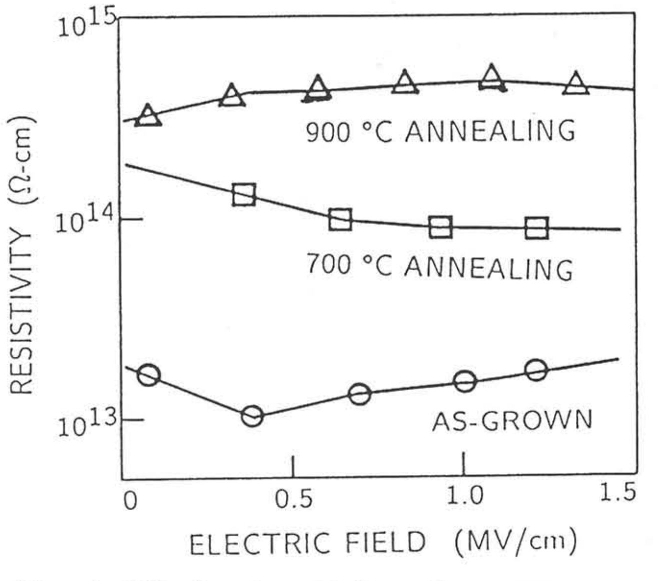

Fig. 4: Effects of rapid thermal annealing on Ta_2O_5 films resistivity measured as a function of applied electric fields.

5. CONCLUSION

In conclusion, we have succeeded in growing high quality Ta_2O_5 dielectric material from a carbon based liquid source $Ta(OC_2H_5)_5$ by using plasma enhanced CVD technique. Our as grown Ta_2O_5 shows very well defined C-V characteristics with Vfb as low as about -0.1eV for both n,p-Si, dielecric 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. REFRENCES

1) M. Matsui, S. Oka, K. Yamagishi, K. Kuroiwa and Y. Tarui, J.J.A.P. 27(4) (1988) pp. 506-511.
2) K. Yamagishi and Y. Tarui J.J. A. P., 25(4), (1986) pp. L306-308.
3) H. Shinriki, Y. Nishioka, Y. Ohji and K. Mukai, IEEE Transaction on Electron Devices 36(2), (1989) pp.328-332.
4) TRI Chemical Laboratory Inc., Japan.
5) M. Saitoh, T. Mori and Tamura, IEDM-86, IEEE,(1986) pp.680-683.
6) U. Teravaninthorn, Y. Miyahara and T. Morizumi J.J.A.P. 26(12), (1987), pp 2116-2120.
7) I. Watanabe and H. Yoshihara J.J.A.P. 24(6),(1985),pp.L411-413.
8) S.Tanimoto, M. Matsui, N. Aoyagi, K. Kamisako, K.Kuroiwa and Y.Tarui, Proc. Int. Conf.SSDM,Sendai,(1990).pp.L195-198.
9) Y. Numasawa, S. Kamiyama, M. Zenke, and M. Sakamoto IEDM 89. (1989) pp 43-46.
10) P.A. Murawala, M. Sawai, T. Tatsuta, O. Tsuji, Sz. Fujita and Sg. Fujita Presented at MRS Spring Meeting, 1992.