Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 195-198

C-2-10

Tantalum Oxide Films Formed by UV Photo-CVD Using Oxygen and Ozone and Its Photo-Chemical Leakage Current Reduction Mechanism

Satoshi TANIMOTO, Masahiro MATSUI, Minoru AOYAGI, Koichi KAMISAKO, Koichi KUROIWA and Yasuo TARUI

Department of Electronic Engineering, Tokyo University of Agricalture and Technology, 2−24−16, Nakamati, Koganei, Tokyo 184, Japan

We developed a new method of fabricating thin films of high dielectric constant Ta_2O_5 through the use of UV photo-CVD, based on the mechanism of a photo-CVD technique presented previously. This type of CVD features the use of $TaCl_5$(6N) and O_2 gas containing extremely pure O_3 gas. The films obtained showed very low leakage current and remarkably good step-coverage at a low temperature of 300 °C with no additional annealing. UV irradiation is essential to improve dielectric breakdown endurance of the film. This new CVD method or understanding on the related mechanism may be applicable to fabrication technology for future VLSI's.

1. Introduction

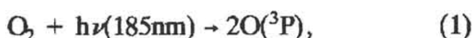
There has been a great deal of interest lately in Ta_2O_5 films because of their potential for use as capacitor dielectrics in DRAMs. [1] Recently sputtered Ta_2O_5 films have been demonstrated to be applicable as storage dielectrics. [2] From the viewpoint of step-coverage, however, CVD seems preferable to sputtering for the formation of storage dielectrics.

In 1987 at the 19th conference on SSDM, The authors demonstrated that low leakage Ta_2O_5 films had been developed by means of UV photo-CVD using $TaCl_5$ and O_2 gas as source materials, followed by UV irradiating annealing in an O_2 ambient at atmospheric pressure. [3]

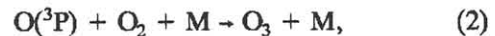
In this paper a new, simple process which produces a low leakage current is described. This new method, that of photo-CVD using O_3 and $TaCl_5$ as source materials, was based on the earlier method using photo-CVD, [4] as will be described in the next section.

2. Concept of Photo-CVD using Ozone

As was described in the previous report, [4] in the annealing of the photo-CVD films using O_2 and $TaCl_5$, active oxygen species such as $O(^3P)$, ozone, $O(^1D)$ and $O_2(^1\Delta)$ play an important role. These were generated by the following multiple reactions initiated by UV photolysis of O_2: [5]



$$O_2 + h\nu(185nm) \rightarrow 2O(^3P), \qquad (1)$$



$$O(^3P) + O_2 + M \rightarrow O_3 + M, \qquad (2)$$

$$O_3 + h\nu(254nm) \rightarrow O(^1D) + O_2(^1\Delta), \qquad (3)$$

$$O_3 \rightarrow O(^3P) + O_2, \qquad (4)$$

where $h\nu$(185nm) and $h\nu$(254nm) are the UV photon energies of the low pressre mercury lamp and M is an oxygen molecule. Such annealing can be thought as *active oxygen annealing* because UV light contributes to the generation of active oxygen species but not to direct reaction with a Ta_2O_5/Si system. [4] Recently Shinriki and others, [6] and Isobe and Saitoh [7] have observed similar leakage current reductions for LPCVD Ta_2O_5 films by performing annealing in UV+O_3, and O_3 ambients, respectively. This supports the above understanding and shows that active oxygen annealing is also effective for LPCVD films deposited under properly selected conditions. In photo-CVD using O_2 and $TaCl_5$ and subsequent active oxygen annealing, the UV 254nm light intensity of the first stage photo-CVD strongly affects the leakage reduction of the second stage active oxygen annealing. [8] This phenomenon can be explained as follows: The exitation and/or photolysis of $TaCl_5$ by 254 nm light(See Fig.1) is important for some *precusor* formation which is effectively annealed by second-stage active oxygen annealing. This fact indicates the importance of activation due to UV light during the deposition, especially at low temperature. A current reduction mechanism for the photo-CVD films using O_2 and $TaCl_5$ is schematically shown in Fig.2(a).

The new type of photo-CVD, shown in Fig.2(b), is

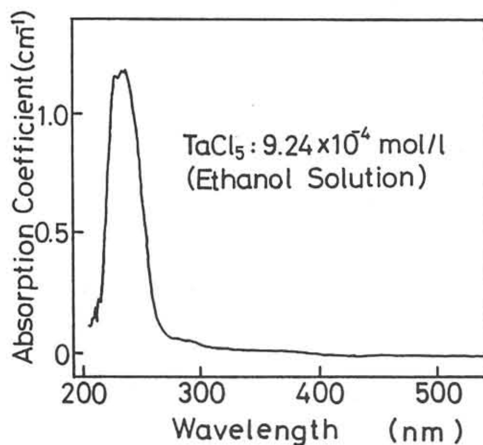


Fig.1 Absorption spectra of $TaCl_5$ dissolved in ethanol in the visible and ultraviolet wavelength regions (after ref.4).

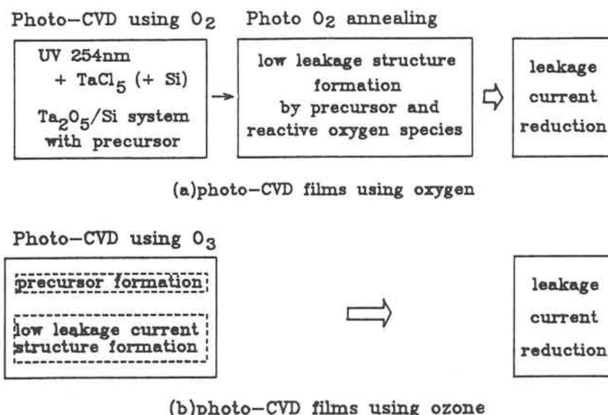


Fig.2 Block diagrams to explain current reduction mechanism by two photo processes: photo-CVD using (a)O_2 and $TaCl_5$, and (b)O_3 and $TaCl_5$.

based on the idea that both precursor formation and active oxygen annealing will be performed in the deposition at the same time. The key point is the use of ozone gas as an oxidant source. When O_2 is used, it is difficult to produce an appreciable number of active oxygen species during CVD since all of them are produced by multiple reactions initiated from photoreaction (1), which is significantly restrained by the small photo-absorption cross section of O_2 and the small intensity of the 185 nm line of a Hg lamp. However, when O_3 is used, an abundant supply of active oxgen species is expected in CVD because O_3 itself is a reactive species as well as a reactant to other active species, as described in reactions (3) and (4). Photo absorption cross sections for O_2 and O_3, σ_n are cited in Table 1. [5)] Note that O_3 has 10^4 times as large a photo-absorption cross section as O_2 and, for photolysis (3), the 254 nm Hg lamp line is utilized which is about ten times stronger than the 185 nm line. In order to estimate the number of active oxygen species during deposition, the amount of UV photo-absorption per unit area in a practical CVD chamber, $(I_0-I)/I_0$, was calculated for photo-CVD using O_2 gas containing 5 vol% O_3, assuming the typical CVD conditions described in the following section and disregarding thermal dissociation for simplicity. Here I_0 and I are light intensities at the positions just under the window and of the substrate, respectively. The results are also listed in Table 1. It can be seen that only 5 vol% ozone could efficiently absorb the incident 254 nm emission line by 4.7% and generate the active oxygen species $O(^1D)$ and $O_2(^1\Delta)$ through the reaction (3), and that on the other hand, absorption in the 185 nm and 254 nm line by O_2 would be as low as to be insignificant.

3. Deposition and Measurement

Thin Ta_2O_5 films with thicknesses of about 40 nm were grown on n-type single crystalline Si(1−3Ωcm,<100>) substrates by UV photo-CVD using $TaCl_5$(6N) and O_2 gas, containing extremely pure O_3 gas. At no time was any additional annealing performed. A schematic diagram of the deposition system is shown in Fig.3. The CVD chamber was constructed of stainless steel. Wavelength emmissions of 185 nm and 254 nm from a low-pressure mercury lamp were irradiated on the substrate surface through a synthetic quartz window (suprasil). UV light intensities were 2.15 mW/cm^2 for 185 nm and 20.3 mW/cm^2 for 254 nm just under the window. The distance between the window and the substrate was 79 mm. O_3 with concentration of from 0 to 7 vol% and free from metal contanimation was induced from O_2 by a QNA-1M silent discharge-type ozone generator (Nippon Ozone Co.,Ltd), and introduced into the chamber. $TaCl_5$ vaporized in a sublimator at 68 °C and N_2 carrier gas (10 sccm) were piped together through the sus-304 tube leading to the chamber and then diffused onto Si substrates from a multi-head nozzule mounted above them. This tube for $TaCl_5$ was kept at a temperature of 160 °C to prevent re-condensation. Depositions typically were carried out under the conditions listed in Table 2. Under these conditions, the deposition rate was approximately 4.0 nm/min. The thickness of the Ta_2O_5 films was determined by utilizing ellipsometry.

Al electrodes with an area of 2.4×10^{-3} cm^2 were formed on the Ta_2O_5 films to measure the current-

Table 1 Calculation results of amount of UV photo-absorption by O_2 and O_3 in reaction chamber during CVD, assuming the deposition conditions shown in Table 2. Values of absorption cross sections (σ_n) of O_2 and O_3 were from ref.5. λ and n are concentration of oxygen species and emmision wavelength of Hg lamp, respectively.

gas	λ[nm]	σ_n[cm^2/molec]	n[1/cm^3]	$(I_0-I)/I$[%]
O_2	185	1.9×10^{-22}	2.6×10^{16}	4.0×10^{-3}
(95vol%)	254	1.7×10^{-24}	2.6×10^{16}	4.0×10^{-5}
O_3	185	6.3×10^{-19}	1.2×10^{15}	0.63
(5vol%)	254	4.8×10^{-18}	1.2×10^{15}	4.7

Table 2 Typical depositions conditions of UV photo-CVD using O_3 and $TaCl_5$.

deposition parameters		values
source materials	$TaCl_5$	68 ℃,
	(N_2 carrier	10 sccm)
	O_2	71.5 sccm
	O_3	3.5 sccm
		4 Torr
substrate tmperature		300 ℃
UV light intesities	185 nm	2.15 mW/cm
	254 nm	20.3 mW/cm
substrate-to-window distance		79 mm

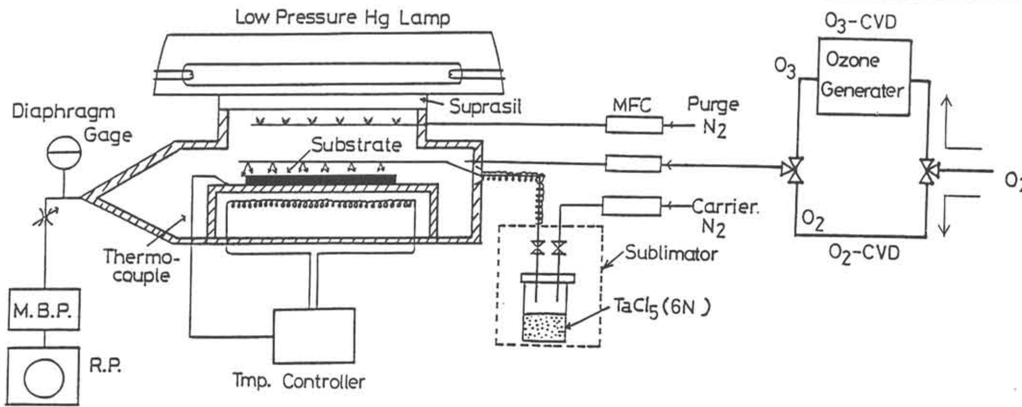


Fig.3 Shematic diagram of the photo-CVD system using ozone gas.

voltage (I-V) and high frequency (1 MHz) capacitance-voltage (C-V) characteristics of the films. The I-V measurements were carried out in an electrical polarity where the metal-insulator-semiconductor capacitor was in the accumulation state.

4. Results and Discussion

Figure 4 shows a typical leakage current density versus electric field ($J-E_{ox}$) characteristic of a Ta_2O_5 film formed by photo-CVD using ozone, along with recently reported data. [4),6),7),9),10)] As can be seen from this figure, the low value of leakage current is attained in the case of photo-CVD using ozone. It should be emphasized that this film was formed at a low temperature of 300 °C with no additional annealing.

The effect of UV light intensity in photo-CVD using O_3 on $J-E_{ox}$ characteristics is shown in Fig.5. From the figure, we can see that UV irradiation in CVD improves the resitivity and the dielectric breakdown strength of films. UV irradiation, therefore, is of importance at least for low-temperature CVD. As mentioned above, O_3 is dissociated into two kinds of active oxygen (reaction (3)) by absorbing the intense 254 nm emmision line of a Hg lamp. It would appear that the more reactive radical of the two, $O(^1D)$ plays an important role in this improvement.

A typical C-V characteristic of Ta_2O_5 film formed by photo-CVD using ozone is shown in Fig.6. All capacitance values are normalized by maximum value in the accumulation region. Positive flatband voltage indicates that small amounts of negative charges exist in Ta_2O_5 film.

A SEM photograph of Ta_2O_5 film deposited on a trench opened in silicon substrate is shown in Fig.7. It is appearent that photo-CVD using $TaCl_5$ and O_2 gas containing ozone can yield good step-coverage.

5. Conclusion

We developed a new UV photo-CVD fabricating thin films of high dielectric constant Ta_2O_5 through the use of UV photo-CVD, based on mechanism of a photo-CVD technique presented previously. This type of CVD features the use of $TaCl_5$ and O_2 gas containing

extremely pure O_3 gas. The films obtained showed very low leakage current and remarkably good step-coverage at a low temperature of 300 °C with no additional annealing. UV irradiation is essential to improve dielectric breakdown endurance of the film. This new CVD method or understanding on the related mechanism may be applicable to fabrication technology for future VLSI's.

References

1)K.Ohta et al.,IEEE Trans.Electron Devices, ED-29,p.368,1982

2)H.Shinriki et al.,Proc.Symp.VLSI Tech.,p.29, 1988

3)Y.Tarui et al.,Extend Abstract of the 19th SSDM, p.219,1987

4)M.Matsui et al.,Jpn.J.Appl.Phys,27,p.506,1988

5)H.Okabe, *Photo-Chemistry of Small Molecules* (John Wiley and Sons Inc.,New York,1978), Chap.V,p.177

6)H.Shinriki et al.,Proc.Symp.VLSI Tech., p.25,1989

7)C.Isobe and M.Saitoh,Appl.Phys.Lett.,56, p.907,1990

8)S.Tanimoto et al,preprint

9)Y.Numazawa et al.,IEEE IEDM Tech.Dig., p.43,1989

10)C.Hashimoto et al.,IEEE Trans.Electron Devices,ED-36,p.14,1989

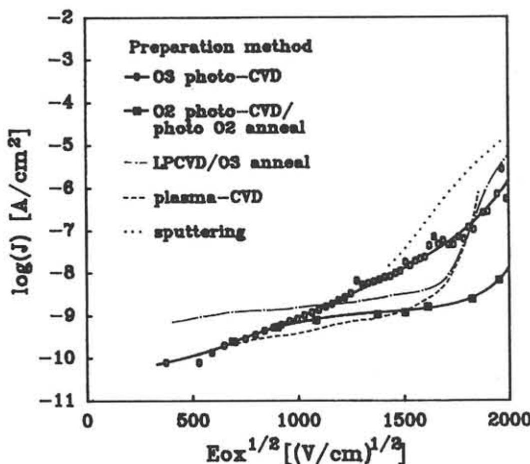


Fig.4 Typical leakage current density versus electric field ($J-E_{ox}$) characteristic of Ta_2O_5 film by photo-CVD using ozone, along with recently reported data

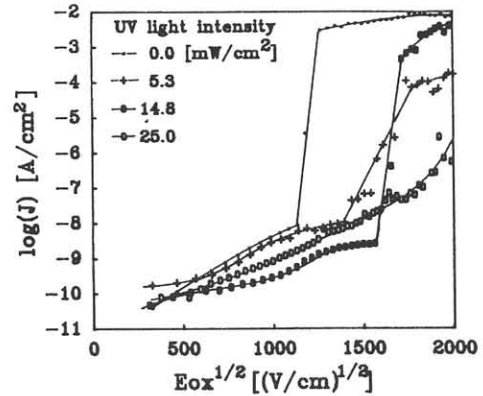


Fig.5 $J-E_{ox}$ characteristics of O_3 photo-CVD Ta_2O_5 films with Hg 254 nm intensity as a parameter. 185 nm emmision was eliminated by mean of optical filter.

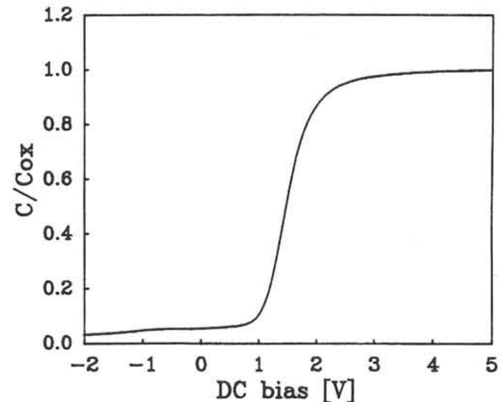


Fig.6 Typical C-V characteristics of an $Al/Ta_2O_5/Si$ MIS capacitor formed by photo-CVD using ozone. Capacitance values were normalized by a capacitance value of Ta_2O_5. Frequency was 1 MHz.

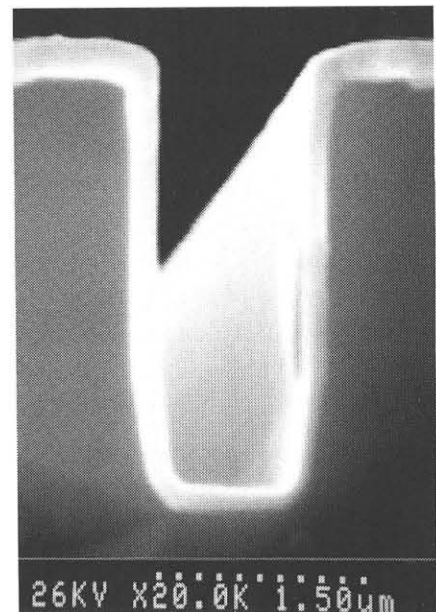


Fig.7 SEM photograph of cross section of Ta_2O_5 film deposited on a trench of Si substrate.