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Photo-CVD of Tantalum Oxide Films and Their Characteristics

Yasuo TARUI, Satoshi OKA, Masahiro MATSUI,
Koji YAMAGISHI* and Koichi KUROIWA
Department of Electronic Engineering, Tokyo University of
Agriculture and Technology, Koganei, Tokyo 184, Japan

TaO_x film formation by a photo-CVD method using $TaCl_5$ as a source material is examined. The deposition rate increases with increasing growth temperature and decreasing chamber pressure down to 1 Torr. Leakage current of the formed TaO_x film decreases drastically with annealing in the presence of both UV-irradiation and an oxygen ambient after deposition(p-O_2 annealing), when the underlying layer containes Si. The leakage current density is 10^{-8} A/cm^2 at the 4 MV/cm electric field. The dielectric constant for MIS structure capacitors decreases with decreasing TaO_x thickness, but it does not decrease much with the p-O_2 annealing.

1. Introduction

To further increase VLSI integration, such as for megabit class MOS DRAM's or low voltage operation of thin film transistors, introduction of a capacitor insulator with higher dielectric constant, instead of the conventional SiO_2, is desirable. Tantalum oxide is a promising material for this purpose because of its high dielectric constant, and has been studied extensively. However, TaO_x films have been considered to be too leaky for practical use, and various methods have been proposed for overcoming this drawback.[1-4]

Previously, growth of TaO_x films by a photo-CVD method using $Ta(OCH_3)_5$ as a source material was examined, and relatively good electrical characteristics were confirmed in the grown films.[5] These films, however, did not have sufficiently high dielectric breakdown strength, probably because of carbon contamination from $Ta(OCH_3)_5$. To avoid this contamination, a photo-CVD method using tantalum pentachloride as a source material and additional annealing with UV-irradiation in an oxygen ambient were developed.

*Permanent address: VLSI Development Laboratories of SHARP Corporation, Tenri, Nara 632

2. Formation of TaO_x by photo-CVD from $TaCl_5$

Tantalum pentachloride($TaCl_5$) absorbs light strongly at wavelengths below 280 nm (molar extinction coefficient is 498 $l\cdot mol^{-1}\cdot cm^{-1}$ at 254 nm). Light irradiation from a low pressure Hg lamp with resonance lines at 254 nm and 185 nm activates $TaCl_5$ and forms TaO_x film by oxidation in the presence of oxygen. The reactive O radical produced by the following photo-chemical reaction[6] also assists TaO_x formation.

$$3O_2 \rightarrow 2O_3 \ (<195 \text{ nm}), \quad O_3 \rightarrow O+O_2 \ (200\text{-}300 \text{ nm})$$

The photo-CVD system is shown schematically in Fig.1. The 254 nm and 185 nm wavelength ultraviolet light from a low pressure Hg lamp irradiates a substrate through a synthetic quartz window (Suprasil). The intensity of the 254 nm light is about 40 mw/cm^2 at the substrate position. The intensity of the 185 nm light is about 15 % that of the 254 nm light. $TaCl_5$ has a low vapor pressure at room temperature, so it is vaporized at 120 °C and carried into the

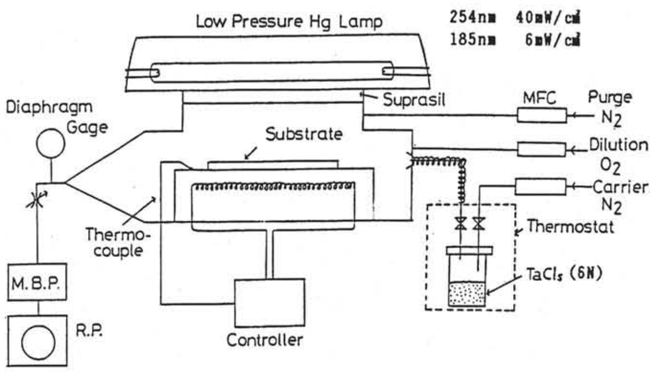

Fig.1. Schematic diagram of the photo-CVD system.

chamber in a nitrogen stream. N-type (100) silicon wafers were usually used as substrates. In MIM capacitor fabrication, CVD tungsten-silicide annealed in a nitrogen ambient at 850 °C after tungsten deposition, and other metals (Cr, Ti) or metal-alloy (TiW) were used as materials for the underlying layer.

Growth temperature dependence of the deposition rate and refractive index of the formed TaO_x film is shown in Fig.2. The deposition rate increased with increasing deposition temperature and decreasing chamber pressure down to 1 Torr. TaO_x film formation was very slow (less than 2 A/min at 400 °C) without light irradiation, and thus such irradiation was found to enhance the deposition rate and enable TaO_x film growth at even lower temperatures. To check the effects of the reactive O radical production by 185 nm light on the deposition rate, TaO_x film was deposited using a quartz window, the transmittance of which is much lower for 185 nm light than that of Suprasil windows. In this case the deposition rate was less than one third of that in the Suprasil case. This result indicates that reactive O radical production may be effective for the oxidation reaction of $TaCl_5$.

The refractive index of the photo-CVD film was constantly about 2.2 at a growth temperature above 300 °C, which is close to

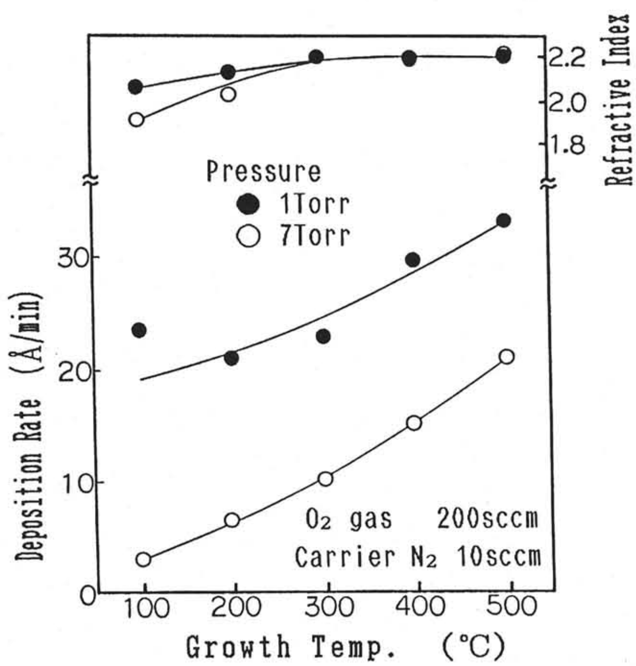

Fig.2. Growth temperature dependence of the deposition rate and the refractive index of TaO_x.

the value of bulk Ta_2O_5. It gradually decreased as the growth temperature was lowered.

3. Electrical properties of photo-CVD TaO_x film

Current-voltage (I-V) characteristics of the Al(+)/TaO_x/n-Si structure are shown in Fig.3. TaO_x films were formed at a growth temperature of 300 °C and annealed at 400 °C in various ambients. The annealing was done in the same chamber as shown in Fig.1. Leakage current of TaO_x film could be drastically decreased only when it was annealed in the simultaneous presence of both UV-irradiation and oxygen ambient (henceforth denoted as p-O_2 annealing). The effect of this p-O_2 annealing was reduced drastically by replacing the Suprasil window with a quartz one. This means that 185 nm light plays an important role in p-O_2 annealing.

Concerning p-O_2 annealing conditions, the leakage current of TaO_x film was decreased by increasing annealing time,

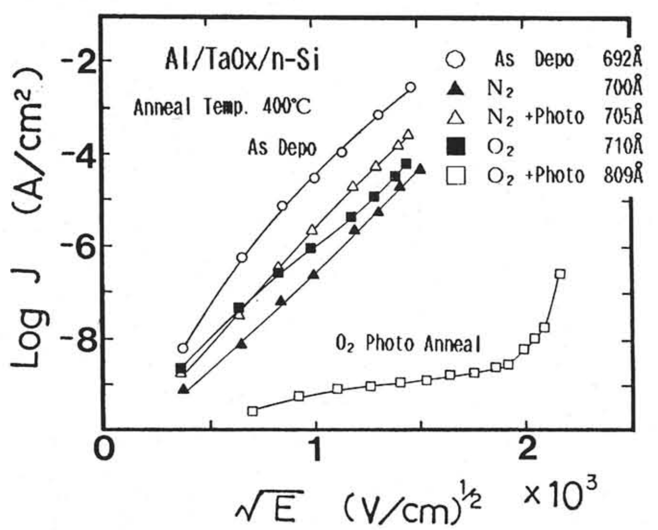

Fig.3. Current-voltage characteristics of TaO_x before and after annealing in various ambients. Growth temperature was 300 °C, and annealing temperature was 400 °C.

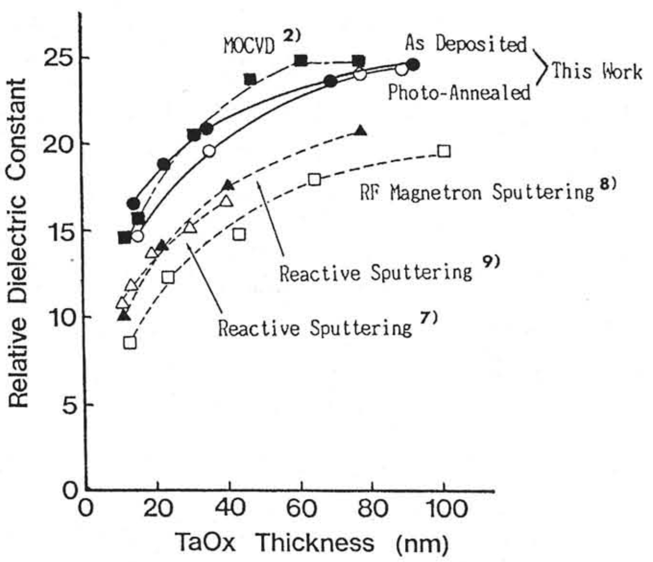

Fig.4. Thickness dependence of the dielectric constant of TaO_x film formed on Si by various methods.

substrate temperature and oxygen pressure in the chamber. There was, however, no additional decrease for annealing times of more than one hour, and even a slight increase when the substrate temperature exceeded 400 °C. Consequently, the optimum values of annealing time, oxygen pressure and substrate temperature were selected to be 1 hour, 1 atm and 400 °C, respectively. Leakage current density of the p-O_2 annealed TaO_x was 10^{-8} A/cm^2 at the 4 MV/cm electric field.

The p-O_2 annealing was also effective for MIM structure capacitors when the underlying layer of TaO_x film was a material containing Si, such as metal-silicide. However, the effect was small when the underlying layer did not contain Si.

Thickness dependence of the dielectric constant of photo-CVD TaO_x film with and without p-O_2 annealing is shown in Fig.4. They were calculated from the MOS capacitance in the accumulated region at 100 kHz and 1 MHz. The dielectric constant decreased with decreasing TaO_x thickness, but it did not decrease much with p-O_2 annealing. It is noted that the dielectric constants of photo-CVD TaO_x films in this experiment were larger than those previously reported for TaO_x films sputtered on single-crystalline Si[7-9] throughout the whole thickness region.

4. Mechanisms of p-O_2 annealing

As one possible mechanism of the p-O_2 annealing effect, it can be inferred that oxidizing species reduce the density of donor levels in TaO_x film, such as oxygen vacancies, the leakage current source. This is derived from the dependence of the p-O_2 annealing effect on the annealing conditions and window materials.

Silicon, however, should take part in the p-O_2 annealing effect because it is dependent on whether or not silicon was contained in the underlying layer, as mentioned earlier.

One possible function of silicon is two-dimensional formation of SiO_2 with a low leakage current but a low dielectric constant compared with TaO_x film. It is not likely, however, to play an important role in the reduction of leakage current after p-O_2 annealing. This is because the change in dielectric constant during p-O_2 annealing is quite small and the estimated thickness of the formed SiO_2 is only a few angstrom.

Differences in distribution and chemical states of principal elements (Si, Ta, O) in TaO_x film between before and after p-O_2 annealing were investigated. Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used for the two specimens. Typical results of SIMS employing an Ar^+ primary ion beam are shown in Fig.5. The most significant change after p-O_2 annealing was the increase in silicon ion intensity from the TaO_x film.

This phenomenon was also observed from XPS data, where a Si*2p* peak of oxide(SiO_x) was detected from the surface of only the p-O_2 annealed TaO_x film, together with a Ta*4f* peak of Ta_2O_5.

The following processes are hypothesized from these SIMS and XPS results. During p-O_2 annealing, silicon atoms diffuse from the substrate into the overlaying TaO_x film, and are substituted for tantalum atoms in the TaO_x lattice or changed into oxide in TaO_x

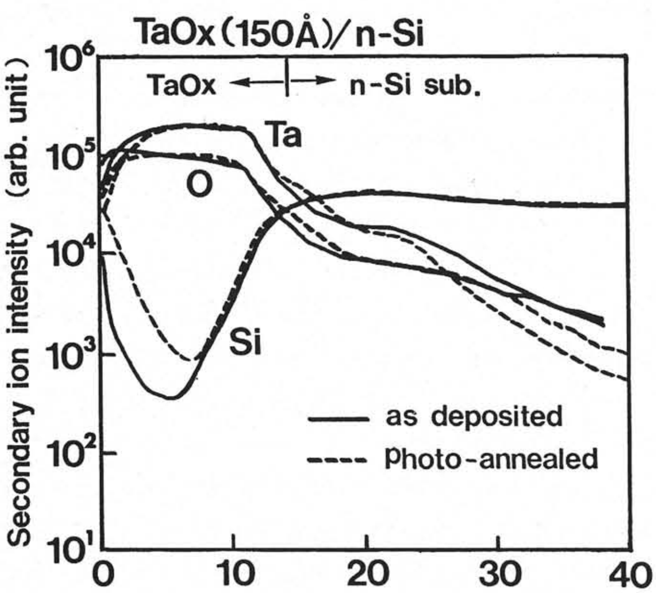

Fig.5. SIMS depth profiles of Si, Ta, O for 150 A thick TaO_x films on Si substrates before and after p-O_2 annealing. Ar^+ ions were used for primary beams.

film. Consequently, it seems that the leakage paths are filled in or oxygen vacancies are reduced.

The reduction of the leakage current after p-O_2 annealing may be explained by the functions of both oxidizing species and silicon atoms diffusing into TaO_x film.

5. Conclusion

TaO_x films were deposited by a photo-CVD method using $TaCl_5$ as a source material. It was found that p-O_2 annealing is a promising method for fabrication of TaO_x film with low leakage current and high dielectric constant because it is not accompanied by a significant decrease in dielectric constant.

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