

# Effect of deposition temperature on dielectric properties of PECVD Ta<sub>2</sub>O<sub>5</sub> thin film

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Tantalum oxide film formation by plasma-enhanced chemical vapour deposition (PECVD) using TaCl<sub>5</sub> as a source material was examined. The effects of deposition temperature on the formation, structure and electric properties of the Ta<sub>2</sub>O<sub>5</sub> film were investigated for Al/Ta<sub>2</sub>O<sub>5</sub>/p-Si (MTS) capacitors. The deposition rate and refractive index increased with increasing deposition temperature. It was found that the structure of Ta<sub>2</sub>O<sub>5</sub> deposited by PECVD was amorphous as-deposited. However, crystalline δ-Ta<sub>2</sub>O<sub>5</sub> of hexagonal structure was formed by a 700 °C, 1 h heat treatment in argon. Capacitance and relative dielectric constant of the PECVD Ta<sub>2</sub>O<sub>5</sub> were found to be 2.54 fF μm<sup>-2</sup> and 23.5, respectively. The PECVD films obtained in this study have higher dielectric constants and remarkably better general film characteristics than those obtained by other deposition methods.

## 1. Introduction

Development of high-density MOS dynamic random-access memory (DRAM) devices with small cell areas has been accomplished by reducing the thickness of the SiO<sub>2</sub> storage capacitors to maintain the required charge storage level. However, the reduction of the SiO<sub>2</sub> insulator thickness is going to approach the physical limit in future very-large-scale integrated circuits (VLSIs). There is great interest in Ta<sub>2</sub>O<sub>5</sub> films because of their potential applications as dielectric films to storage capacitors in memory cells and gate insulators [1–3] in VLSIs circuits. Although tantalum oxide has a high dielectric constant (22–28) [4–6], it has been considered too leaky for practical uses. Deposition methods using anodic oxidation [7], thermal oxidation [8, 9], r.f. sputtering [10], and chemical vapour deposition (CVD) [11–15] have been investigated to various extents to overcome this drawback, but the problem persists. In the present work, for the application of Ta<sub>2</sub>O<sub>5</sub> to silicon devices as a storage capacitor, it was necessary to perform a fundamental investigation into a mono dielectric layer. Dielectric Ta<sub>2</sub>O<sub>5</sub> thin films were prepared by PECVD on p-type silicon substrates. The effects of substrate temperature on formation, structure, stoichiometry attainment, and electrical properties of the Ta<sub>2</sub>O<sub>5</sub> films were investigated for Al/Ta<sub>2</sub>O<sub>5</sub>/p-si capacitors.

## 2. Experimental procedure

Ta<sub>2</sub>O<sub>5</sub> films from 60–90 nm thick were grown on (1 0 0) p-type silicon (5 Ω cm) substrates by PECVD. A

pure inorganic tantalum source, TaCl<sub>5</sub> (99.999%), was used to eliminate carbon contamination in the films in order to improve current–voltage characteristics. A schematic diagram of the apparatus is shown in Fig. 1. The tantalum was vapourized at 100 °C using argon as a carrier gas, and passed into the plasma reactor with the argon from the vapourizer through a heating line. The heating line was kept at a temperature of 160 °C to prevent recondensation of TaCl<sub>5</sub>. Prior to deposition, the chamber was evacuated to a background pressure of < 1 × 10<sup>-4</sup> Pa. Then, for reaction, the chamber pressure was maintained at 79.7 Pa (0.60 torr). In order to obtain good-quality Ta<sub>2</sub>O<sub>5</sub> film, the substrate temperature was varied to optimize deposition. The experimental conditions are listed in Table I. Electrical measurements were conducted on Al/Ta<sub>2</sub>O<sub>5</sub>/p-Si (MTS) capacitors.

The refractive index and thickness of the Ta<sub>2</sub>O<sub>5</sub> films formed by the PECVD were determined by

TABLE I PECVD conditions

Deposition parameters	
Ar carrier gas flow rate	10 standard cm <sup>3</sup> min <sup>-1</sup>
N <sub>2</sub> O gas flow rate	25 standard cm <sup>3</sup> min <sup>-1</sup>
Total gas flow rate	115 standard cm <sup>3</sup> min <sup>-1</sup>
Vapourize temperature	100 °C
Heating line temperature	160 °C
Substrate temperature	300–450 °C
Chamber pressure	79.7 Pa
r.f. power	0.23 ~ 0.71 W cm <sup>-2</sup>

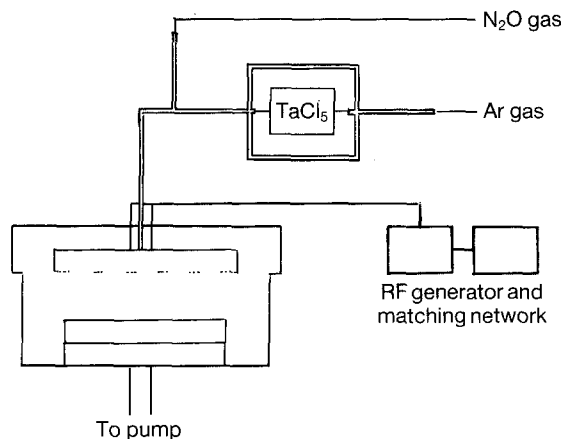


Figure 1 Schematic diagram of the plasma-enhanced chemical vapour deposition apparatus.

ellipsometry at 632.8 nm wavelength. The structure of the  $\text{Ta}_2\text{O}_5$  films was investigated by X-ray diffraction (XRD) with a nickel-filtered copper target at 35 kV and 29 mA. The chemical structure of the  $\text{Ta}_2\text{O}_5$  films on silicon was analysed by X-ray photoelectron spectroscopy (XPS). Depth profiles of the  $\text{Ta}_2\text{O}_5$  films were obtained by Auger electron spectroscopy (AES) with an argon ion gun and measurements were carried out at a 3 kV electron excitation voltage and a 2 kV sputtering voltage. To observe  $\text{Ta}_2\text{O}_5$  film thickness, structure and the  $\text{Ta}_2\text{O}_5/\text{Si}$  interface, cross-sectional transmission electron microscopy (XTEM) was performed at 400 kV. Capacitance–voltage measurements were performed at 1 MHz using a HP4280A  $C-V$  plotter. The dielectric constant of the film was calculated from the capacitance at the accumulation region. The leakage current was measured by the d.c. ramp method with a ramp rate of  $0.1 \text{ V s}^{-1}$  and a negative gate voltage using a HP 4145B semiconductor parameter analyser.

### 3. Results and discussion

The effect of substrate temperature on various characteristics of  $\text{Ta}_2\text{O}_5$  thin films was investigated. First, structure of the films was analysed in terms of post-annealing temperature. Fig. 2 shows the XRD pattern of the tantalum oxide films which were heat treated at different temperatures for 1 h in an argon atmosphere. Amorphous  $\text{Ta}_2\text{O}_5$  thin films were obtained both for the as-deposited condition and for the annealed condition of  $600^\circ\text{C}$  1 h in an argon atmosphere. However, crystalline thin films were obtained after post-annealing above  $700^\circ\text{C}$ .  $c$ -axis oriented  $\delta\text{-Ta}_2\text{O}_5$  with hexagonal structure was obtained at higher temperatures. Fig. 3 shows the effect of deposition temperature on deposition rate and refractive index. The growth rate was defined as the deposited thickness divided by the deposition time; it shows an almost linear relationship with temperature. The reaction mechanism was proved to be surface-reaction controlled, which depended on chemical reactions on the substrate surface. The apparent activation energy obtained was about  $17.3 \text{ kJ mol}^{-1}$ , which is much lower

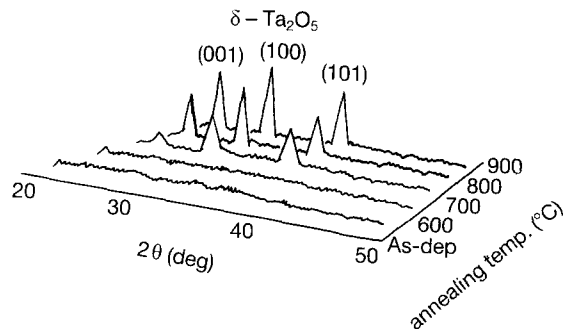


Figure 2 X-ray diffraction pattern of tantalum oxide film after heat treatment for 1 h in argon.

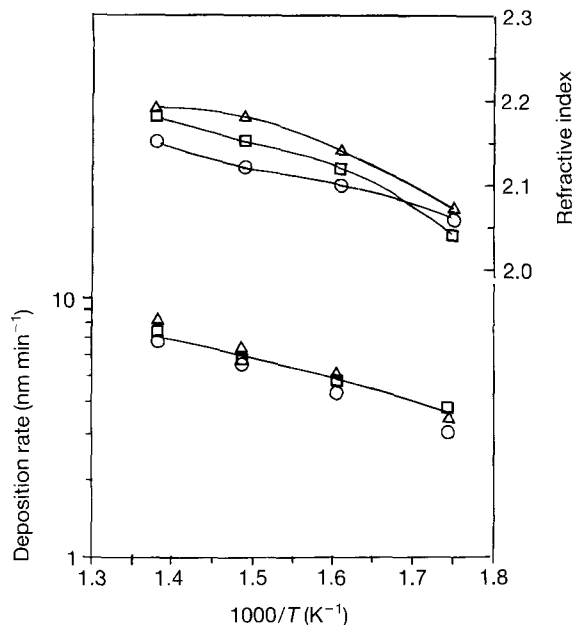


Figure 3 The dependence of deposition rates and refractive index on deposition temperature. R.F. power ( $\text{W cm}^{-2}$ ): ( $\circ$ ) 0.23, ( $\square$ ) 0.47, ( $\triangle$ ) 0.71.  $\Delta E_{\text{app}} = 17.3 \text{ kJ mol}^{-1}$ ; Ar(carrier) = 10 standard  $\text{cm}^3 \text{ min}^{-1}$ ;  $\text{N}_2\text{O} = 25$  standard  $\text{cm}^3 \text{ min}^{-1}$ ; pressure = 79.7 Pa.

than the values obtained by the conventional LPCVD method.

The refractive index approached the theoretical value of 2.2 as the deposition temperature increased, which might be due to both easy formation of dense films by radical adsorption during the deposition reaction and easy desorption of by-products as the temperature increases.

The current–voltage ( $I-V$ ) characteristics of the  $\text{Al}/\text{Ta}_2\text{O}_5/\text{p-Si}$  structure are shown in Fig. 4.  $\text{Ta}_2\text{O}_5$  films were formed at  $300\text{--}450^\circ\text{C}$  and annealed at  $600^\circ\text{C}$  in an argon atmosphere. Aluminium was deposited after each annealing treatment in order to avoid any reaction between the  $\text{Ta}_2\text{O}_5$  film and aluminium during annealing. The leakage current of  $\text{Ta}_2\text{O}_5$  could be drastically improved only when it was annealed in argon ambient. It was clear that the annealed PEVCD  $\text{Ta}_2\text{O}_5$  films were denser than as-deposited ones. The relationship between dielectric constant of the films and the deposition temperature is shown in Fig. 5. The dielectric constants were calculated from capacitance values in the accumulation region of the 1 MHz  $C-V$  curve. The values obtained

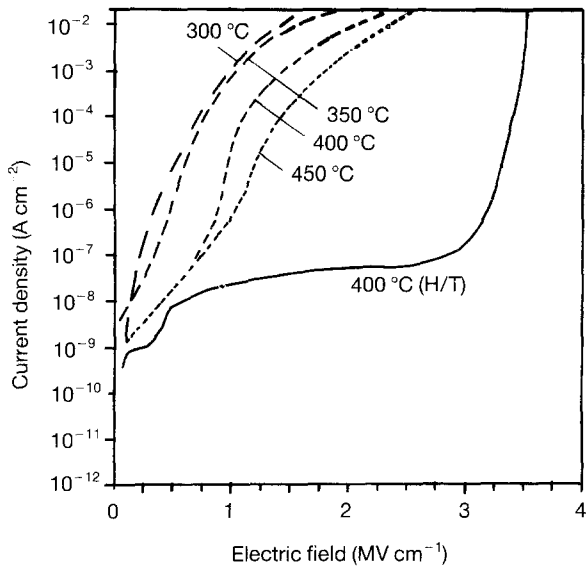


Figure 4 The effect of deposition temperature on the  $I-V$  characteristics of Al/Ta<sub>2</sub>O<sub>5</sub>/p-Si as-deposited.

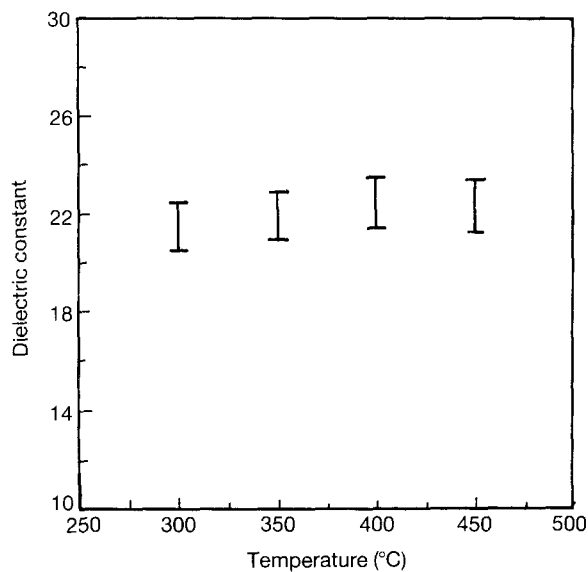


Figure 5 The dependence of dielectric constant on deposition temperature of Al/Ta<sub>2</sub>O<sub>5</sub>/p-Si. Ar(carrier) = 10 standard cm<sup>3</sup> min<sup>-1</sup>; N<sub>2</sub>O = 25 standard cm<sup>3</sup> min<sup>-1</sup>; R.F. power = 0.47 W cm<sup>-2</sup>; pressure = 79.7 Pa.

ranged from 20.5–23.5. No noticeable dependency on the deposition temperature was observed.

In order to investigate the chemical stability of Ta<sub>2</sub>O<sub>5</sub> thin films made by various methods, XPS analysis was utilized. Fig. 6 shows the XPS spectra of E-beam Ta<sub>2</sub>O<sub>5</sub>, thermal oxidation Ta<sub>2</sub>O<sub>5</sub>, and PECVD Ta<sub>2</sub>O<sub>5</sub>, as well as metallic tantalum, 4<sub>f<sub>7/2</sub></sub> and 4<sub>f<sub>5/2</sub></sub> peaks of metallic tantalum were 21.8 and 23.6 eV, respectively. When metallic tantalum is combined with oxygen, 4<sub>f<sub>7/2</sub></sub> and 4<sub>f<sub>5/2</sub></sub> peaks tend to shift to the higher binding-energy side. In the case of PECVD Ta<sub>2</sub>O<sub>5</sub>, 4<sub>f<sub>7/2</sub></sub> and 4<sub>f<sub>5/2</sub></sub> peaks of tantalum reside at 27.7 and 29.3 eV, respectively, which shows that more chemically stable films were obtained by PECVD compared with those of the conventional E-beam and thermal oxidation. Ta<sub>2</sub>O<sub>5</sub> films with strong binding energy usually have good dielectric properties [14].

PECVD Ta<sub>2</sub>O<sub>5</sub> shows no carbon residue, which affects leakage properties. Depth profiling of the Ta<sub>2</sub>O<sub>5</sub> thin film was attempted in order to determine compositional variations of the thin films, as shown in

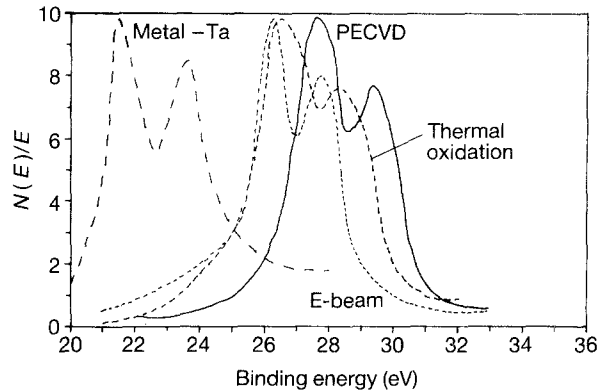


Figure 6 XPS spectra of Ta-O bonding shifts for various methods.

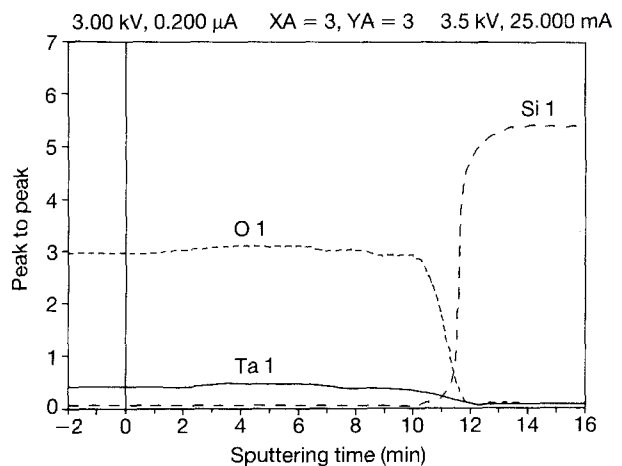


Figure 7 AES depth profile of the Ta<sub>2</sub>O<sub>5</sub> deposited by the PECVD. Ar(carrier) = 10 standard cm<sup>3</sup> min<sup>-1</sup>; N<sub>2</sub>O = 25 standard cm<sup>3</sup> min<sup>-1</sup>; R.F. power = 0.47 W cm<sup>-2</sup>; substrate temperature = 400 °C.

Figure 8 Cross-sectional transmission electron micrograph of Ta<sub>2</sub>O<sub>5</sub> deposited by the PECVD.

Fig. 7. The PECVD Ta<sub>2</sub>O<sub>5</sub> film deposited at 400 °C has a relatively uniform composition throughout the dielectric layer.

Fig. 8 shows a cross-sectional transmission electron micrograph of PECVD Ta<sub>2</sub>O<sub>5</sub> thin films after annealing. The annealing temperature in the range 600–900 °C in an argon atmosphere did not affect the width of the Ta<sub>2</sub>O<sub>5</sub>/Si interface layer, which is thought to be a transition layer of Ta–O/Si–O mixed structure.

#### 4. Conclusion

The structure of as-deposited PECVD Ta<sub>2</sub>O<sub>5</sub> films obtained using TaCl<sub>5</sub> was amorphous. The oxide films were found to have δ-Ta<sub>2</sub>O<sub>5</sub> with hexagonal structure after heat treatment in an argon atmosphere. More stable Ta<sub>2</sub>O<sub>5</sub> was obtained using PECVD than using other conventional deposition methods. The growth rate of the Ta<sub>2</sub>O<sub>5</sub> thin film depended greatly on the substrate temperature, and the deposition mechanism was thought to be surface-reaction controlled. The apparent activation energy of deposition obtained was 17.3 kJ mol<sup>-1</sup>. The leakage currents sharply decreased with increasing post-annealing temperature, and the transition layer of the Ta<sub>2</sub>O<sub>5</sub>/Si interface was unaltered by annealing temperatures in the range 600–900 °C in an argon atmosphere.

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Received 29 September 1992  
and accepted 20 August 1993