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Erratum
Effect of deposition temperature on dielectric properties of PECVD Ta_2O_5 thin film

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Tantalum oxide film formation by plasma-enhanced chemical vapour deposition (PECVD) using $TaCl_5$ as a source material was examined. The effects of deposition temperature on the formation, structure and electric properties of the Ta_2O_5 film were investigated for Al/Ta_2O_5/*p*-Si (MTS) capacitors. The deposition rate and refractive index increased with increasing deposition temperature. It was found that the structure of Ta_2O_5 deposited by PECVD was amorphous as-deposited. However, crystalline δ-Ta_2O_5 of hexagonal structure was formed by a 700 °C, 1 h heat treatment in argon. Capacitance and relative dielectric constant of the PECVD Ta_2O_5 were found to be 2.54 fF μm^{-2} 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_2 storage capacitors to maintain the required charge storage level. However, the reduction of the SiO_2 insulator thickness is going to approach the physical limit in future very-large-scale integrated circuits (VLSIs). There is great interest in Ta_2O_5 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_2O_5 to silicon devices as a storage capacitor, it was necessary to perform a fundamental investigation into a mono dielectric layer. Dielectric Ta_2O_5 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_2O_5 films were investigated for Al/Ta_2O_5/p-si capacitors.

2. Experimental procedure

Ta_2O_5 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, $TaCl_5$ (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 $TaCl_5$. Prior to deposition, the chamber was evacuated to a background pressure of $< 1 \times 10^{-4}$ Pa. Then, for reaction, the chamber pressure was maintained at 79.7 Pa (0.60 torr). In order to obtain good-quality Ta_2O_5 film, the substrate temperature was varied to optimize deposition. The experimental conditions are listed in Table I. Electrical measurements were conducted on Al/Ta_2O_5/p-Si (MTS) capacitors.

TABLE I PECVD conditions

Deposition parameters	
Ar carrier gas flow rate	10 standard $cm^3 min^{-1}$
N_2O gas flow rate	25 standard $cm^3 min^{-1}$
Total gas flow rate	115 standard $cm^3 min^{-1}$
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^{-2}

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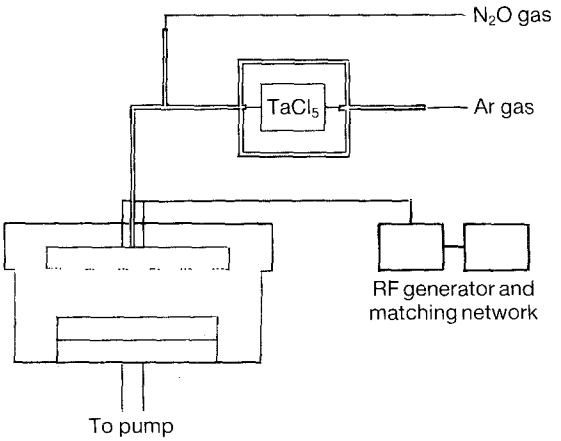

Figure 1 Schematic diagram of the plasma-enhanced chemical vapour deposition apparatus.

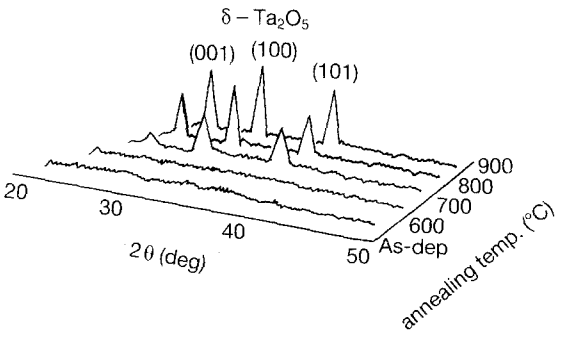

Figure 2 X-ray diffraction pattern of tantalum oxide film after heat treatment for 1 h in argon.

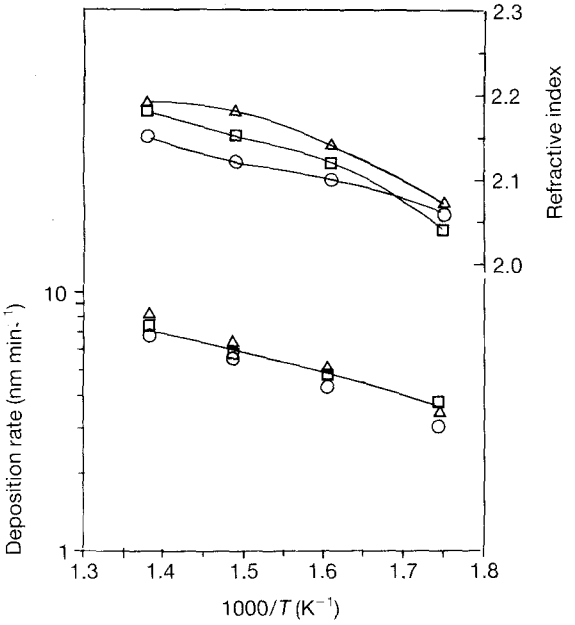

Figure 3 The dependence of deposition rates and refractive index on deposition temperature. R.F. power (W cm^{-2}): (○) 0.23, (□) 0.47, (△) 0.71. ΔE_{app} = 17.3 kJ mol^{-1}; Ar(carrier) = 10 standard cm^3 min^{-1}; N_2O = 25 standard cm^3 min^{-1}; pressure = 79.7 Pa.

The refractive index and thickness of the Ta_2O_5 films formed by the PECVD were determined by ellisometry at 632.8 nm wavelength. The structure of the Ta_2O_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 Ta_2O_5 films on silicon was analysed by X-ray photoelectron spectroscopy (XPS). Depth profiles of the Ta_2O_5 films were obtained by Auger electron spectroscopy (AES) with an argon ion gun and measurements were carried out at a 3 kV electron exitation voltage and a 2 kV sputtering voltage. To observe Ta_2O_5 film thickness, structure and the Ta_2O_5/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 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 Ta_2O_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 Ta_2O_5 thin films were obtained both for the as-deposited condition and for the annealed condition of 600 °C 1 h in an argon atmosphere. However, crystalline thin films were obtained after post-annealing above 700 °C. c-axis oriented δ-Ta_2O_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 kJ mol^{-1}, which is much lower 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 Al/Ta_2O_5/p-Si structure are shown in Fig. 4. Ta_2O_5 films were formed at 300–450 °C and annealed at 600 °C in an argon atmosphere. Aluminium was deposited after each annealing treatment in order to avoid any reaction between the Ta_2O_5 film and aluminium during annealing. The leakage current of Ta_2O_5 could be drastically improved only when it was annealed in argon ambient. It was clear that the annealed PEVCD Ta_2O_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

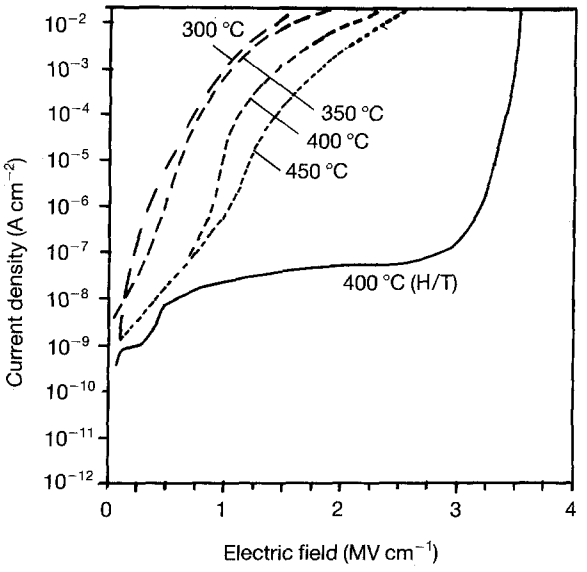

Figure 4 The effect of deposition temperature on the *I–V* characteristics of Al/Ta_2O_5/p-Si as-deposited.

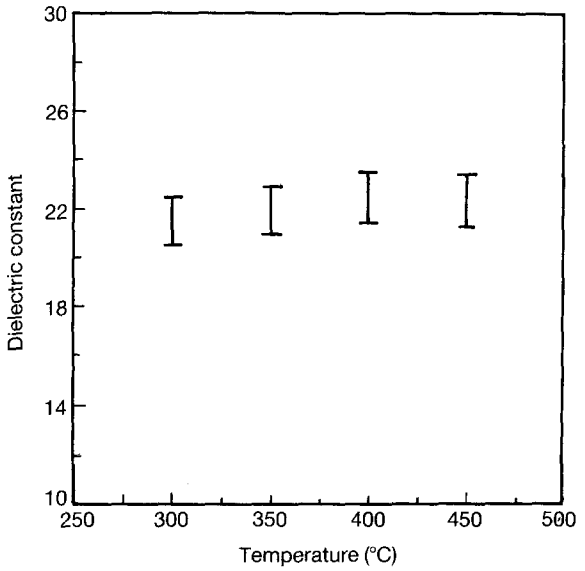

Figure 5 The dependence of dielectric constant on deposition temperature of Al/Ta_2O_5/p-Si. Ar(carrier) = 10 standard cm^3 min^{-1}; N_2O = 25 standard cm^3 min^{-1}; R.F. power = 0.47 W cm^{-2}; pressure = 79.7 Pa.

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

In order to investigate the chemical stability of Ta_2O_5 thin films made by various methods, XPS analysis was utilized. Fig. 6 shows the XPS spectra of E-beam Ta_2O_5, thermal oxidation Ta_2O_5, and PECVD Ta_2O_5, as well as metallic tantalum, $4_{f7/2}$ and $4_{f5/2}$ peaks of metallic tantalum were 21.8 and 23.6 eV, respectively. When metallic tantalum is combined with oxygen, $4_{f7/2}$ and $4_{f5/2}$ peaks tend to shift to the higher binding-energy side. In the case of PECVD Ta_2O_5, $4_{f7/2}$ and $4_{f5/2}$ 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_2O_5 films with strong binding energy usually have good dielectric properties [14].

PECVD Ta_2O_5 shows no carbon residue, which affects leakage properties. Depth profiling of the Ta_2O_5 thin film was attempted in order to determine compositional variations of the thin films, as shown in

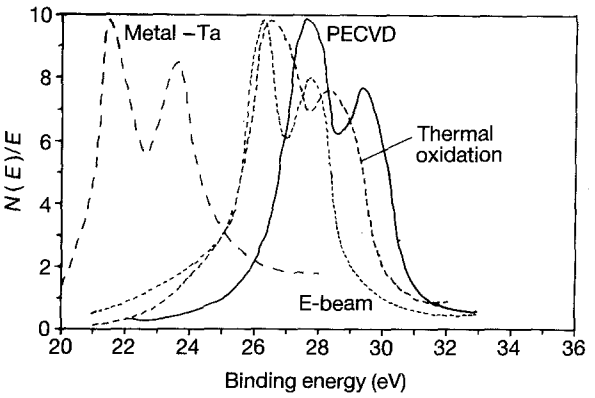

Figure 6 XPS spectra of Ta–O bonding shifts for various methods.

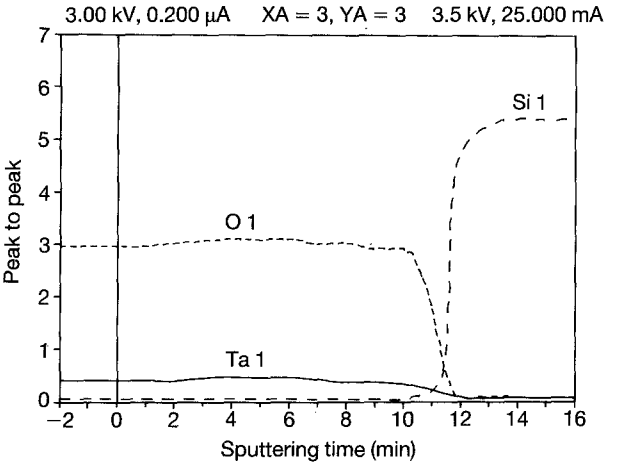

Figure 7 AES depth profile of the Ta_2O_5 deposited by the PECVD. Ar(carrier) = 10 standard cm^3 min^{-1}; N_2O = 25 standard cm^3 min^{-1}; R.F. power = 0.47 W cm^{-2}; substrate temperature = 400 °C.

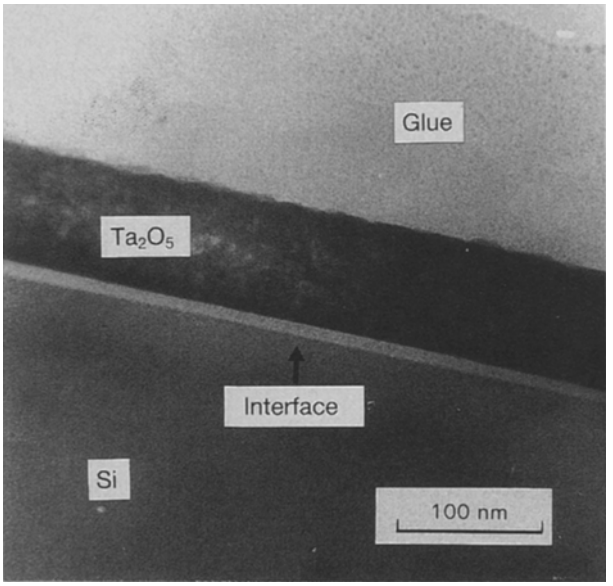

Figure 8 Cross-sectional transmission electron micrograph of Ta_2O_5 deposited by the PECVD.

Fig. 7. The PECVD Ta_2O_5 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_2O_5 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_2O_5/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_2O_5 films obtained using $TaCl_5$ was amorphous. The oxide films were found to have δ-Ta_2O_5 with hexagonal structure after heat treatment in an argon atmosphere. More stable Ta_2O_5 was obtained using PECVD than using other conventional deposition methods. The growth rate of the Ta_2O_5 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^{-1}. The leakage currents sharply decreased with increasing post-annealing temperature, and the transition layer of the Ta_2O_5/Si interface was unaltered by annealing temperatures in the range 600–900 °C in an argon atmosphere.

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