

Metallo–organic compound-based plasma enhanced CVD of ZrO₂ films for microelectronic applications

S CHATTERJEE, S K SAMANTA, H D BANERJEE* and C K MAITI

Department of Electronics & ECE, *Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

MS received 29 January 2001; revised 24 September 2001

Abstract. ZrO₂ films on silicon wafer were deposited by microwave plasma enhanced chemical vapour deposition technique using zirconium tetratert butoxide (ZTB). The structure and composition of the deposited layers were studied by fourier transform infrared spectroscopy (FTIR). The deposition rates were also studied. MOS capacitors fabricated using deposited oxides were used to characterize the electrical properties of ZrO₂ films. The films showed their suitability for microelectronic applications.

Keywords. Zirconium dioxide; high-*k*; PECVD; EOT.

1. Introduction

High dielectric constant (high-*k*) materials have drawn lot of attention, as possible replacements for conventional silicon dioxide (SiO₂) for use as a storage capacitor in ultra large scale integrated (ULSI) circuit memory cells and as gate quality dielectrics for field effect transistors (FETs). High-*k* materials such as Ta₂O₅, TiO₂ and (Ba, Sr)TiO₃ are not thermally stable on silicon and also require a passivation barrier (oxynitride or nitride) to prevent interfacial layer growth (Ngai *et al* 2000). Zirconium dioxide (ZrO₂) is one of the few high-*k* dielectrics predicted to be thermodynamically stable in contact with silicon (Qi *et al* 1999). ZrO₂ was also characterized for low electrical conductivity and chemical inertness (Hubbard and Schlom 1996).

In semiconductor processing, there is a need to minimize the high temperature processing steps for fabrication of circuits/devices with a sub-micrometer feature. Consequently, the use of plasma enhanced chemical vapour deposition (PECVD) technique for film deposition and growth has become attractive, owing to some of its unique features, mainly high plasma density, a wide range of pressure for plasma substance and reduced damage due to low temperature at the substrate (Raoux *et al* 1997; Agnihotri *et al* 2000). In this paper, we present the results of our studies on ZrO₂ film deposition on silicon substrate and their characterization.

2. Experimental

Metallo–organic compounds have been widely used as source materials for deposition of metal oxide on

semiconducting substrate. Zirconium tetratert butoxide [Zr(OC(CH₃)₃)₄] was used as source material for deposition of ZrO₂ films. The experimental setup (figure 1) consisted of a microwave (700 Watt, 2.45 GHz) cavity discharge system within a quartz reactor. Zirconium tetratert butoxide was introduced into the system, independently, from a bubbler (kept at 27°C) on a P-type silicon wafer (5–10 ohm-cm resistivity). Just before the substrate was loaded into the chamber, it was cleaned using conventional process and etched in dilute HF to remove native oxide layer on it. The ZrO₂ films were deposited on the wafer (at 500 mTorr pressure and at 150–200°C temperature). The film thicknesses were measured using a single wavelength (6328 Å) ellipsometer (Model-Gaertner L-117). The electrical properties of the films were studied using MIS capacitors with an Al gate (area: 1.96 × 10⁻³ cm²). The capacitance–voltage (*C*–*V*), conductance–voltage (*G*–*V*) and gate voltage shift (ΔV_g) under constant current stressing were studied using HP-4061A semiconductor test system and HP-4145B parameter analyser, respectively.

3. Results and discussion

The FTIR absorption spectra of a typical ZrO₂ film was recorded using an IR spectrophotometer (Model – Nicolet Magna IR 750) in the wave number scanning range 400–1200 cm⁻¹ (figure 2). Five absorption peaks at wave numbers 474, 530, 575, 630 and 745 cm⁻¹ are observed for ZrO₂ which indicates the formation of ZrO₂ film. This result is in good agreement with the results reported by Balog *et al* (1977). The deposited film also shows a broad band centred at 1065 cm⁻¹, which mainly indicates the presence of Si–O stretching bond. Our extensive FTIR

*Author for correspondence

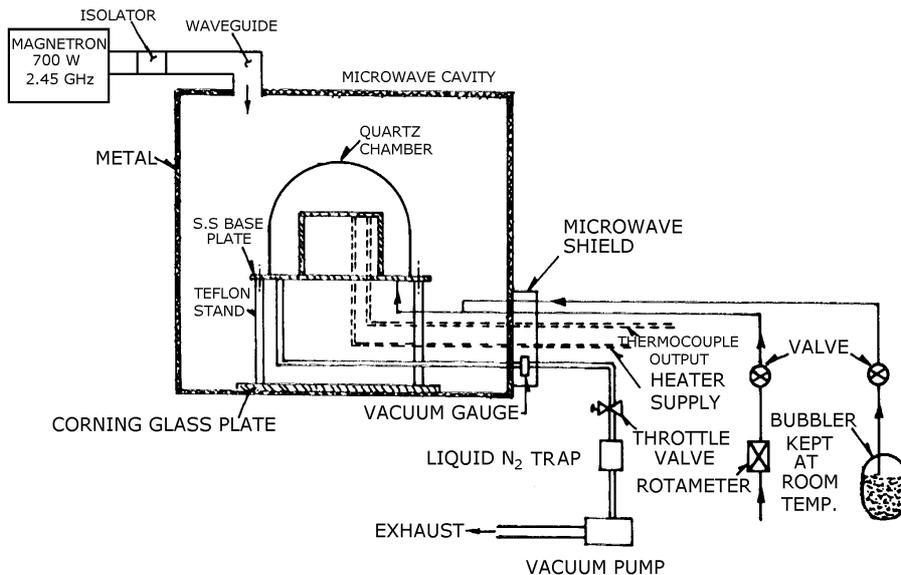


Figure 1. Schematic diagram of plasma enhanced ZrO₂ decomposition system.

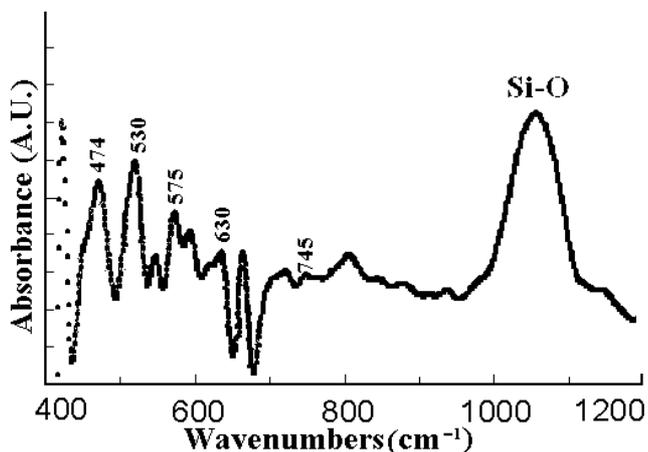


Figure 2. FTIR spectra of ZrO₂ film deposited on Si-substrate.

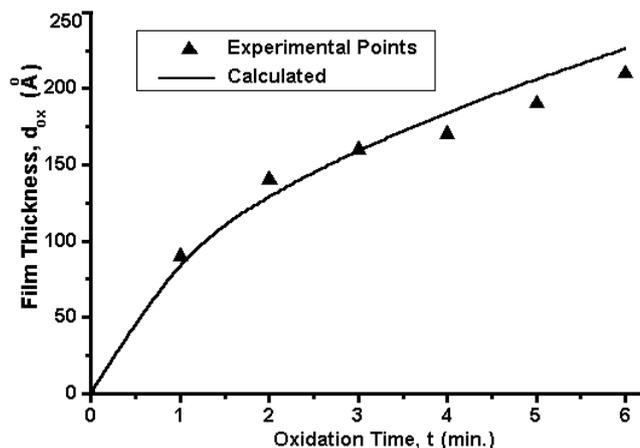


Figure 3. ZrO₂ thickness as a function of time for microwave plasma oxidation. Solid line is calculated using $d_{ox}^2 = B \cdot t$.

studies inferred the existence of ZrO₂ films on the silicon substrate. It was also concluded from such studies that the crystal structure of the material was monoclinic (Cameron and George 1999).

The plot of deposition rate of ZrO₂ film is shown in figure 3. The growth behaviour under the present experimental condition may be described by a parabolic rate equation

$$d_{ox}^2 = B \cdot t, \tag{1}$$

where, d_{ox} is the thickness of oxide grown in time ' t ' and B the parabolic rate constant. The calculated value of B is $8.5 \times 10^3 \text{ \AA}^2/\text{min}$ (Kimura et al 1985).

Figure 4 shows a typically high frequency (1 MHz) C-V characteristics of the film before and after stressing (10 mA cm⁻²). It is observed that for constant current

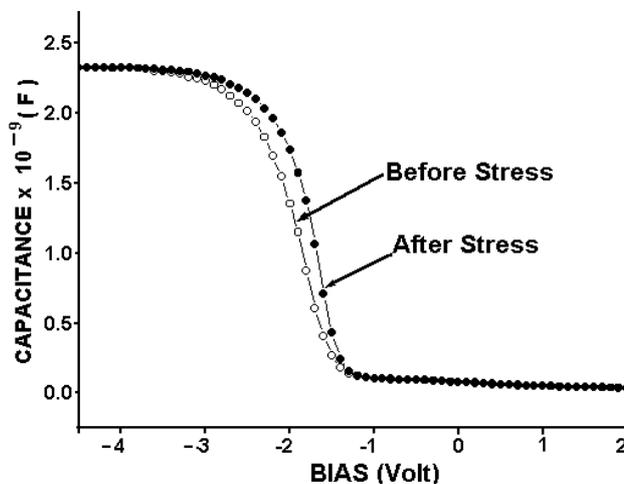


Figure 4. High frequency (1 MHz) C-V characteristics of ZrO₂ films.

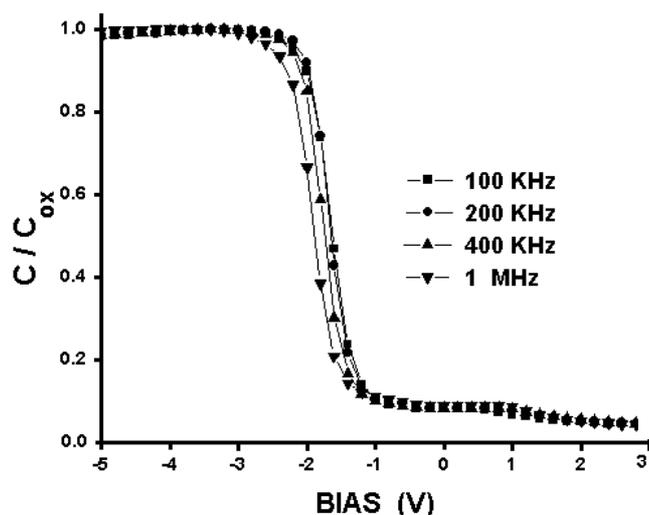


Figure 5. The normalized C - V characteristics at different frequencies.

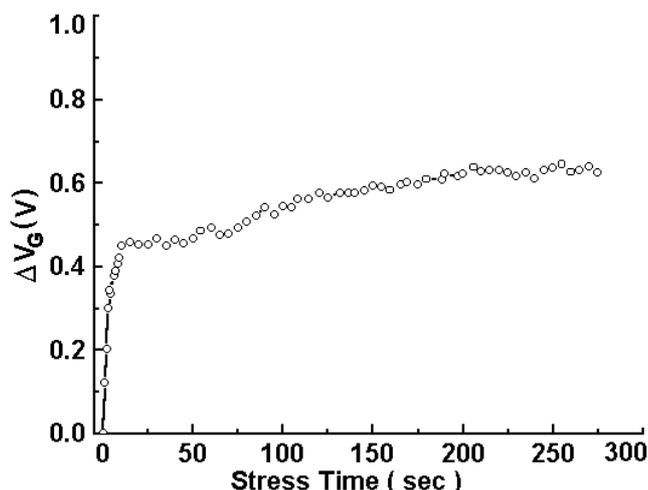


Figure 6. Gate voltage shift vs stress time for ZrO₂ films on Si-wafer under constant current stressing (10 mA cm⁻²).

stressing for 300 s, there is a positive voltage shift which shows the evidence of electron trapping in the dielectric. The dielectric constant was determined from the capacitance-voltage characteristics in the accumulation region of the 1 MHz C - V curves (figure 3) and was found to be ~ 19.7 . Because of high direct tunneling currents, SiO₂ films thinner than 30 Å cannot be used as gate dielectric for CMOS devices (Houssa *et al* 2001).

This difficulty may be avoided using the concept of equivalent SiO₂ thickness (EOT) which is mainly compared to various alternative high- k dielectrics by the equivalent thickness of oxide which would generate the same amount of capacitance/area. In our experiment, the physical thickness of a typical deposited film was ~ 140 Å and the corresponding EOT was ~ 28 Å.

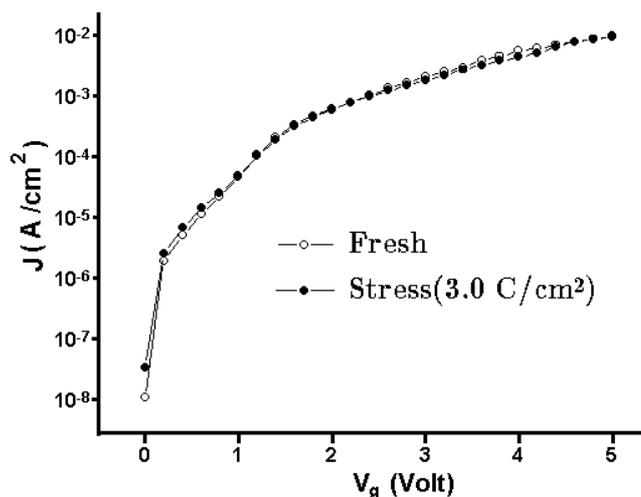


Figure 7. Stress induced leakage currents measurements of ZrO₂ films under 10 mA/cm² current stress.

Figure 5 shows normalized C - V characteristics at different frequencies. Little frequency dispersion is observed, which may be due to the presence of interface charges.

The fixed oxide charge density [$Q_{f/q}$] of the sample is determined as 1×10^{12} cm⁻². The interface trap density (D_{it}) at midgap calculated using Hill's method (Hill and Coleman 1980) is found to be 1.2×10^{12} eV⁻¹ cm⁻².

The charge trapping properties of ZrO₂ films were characterized by the change in gate voltage (ΔV_g) with time under a constant current (10 mA cm⁻²) stressing (figure 6). A moderately high gate voltage shift, ΔV_g , during constant current injection through the gate is attributed to the stress induced electron trap generation.

The results on stress induced leakage current (SILC) measurement is shown in figure 7. No significant SILC was observed under a constant current (10 mA cm⁻²) stressing, showing reasonably low trap generation in the films. Consequently, direct tunneling probability is decreased.

4. Conclusions

The study has demonstrated the low-temperature deposition of ZrO₂ film on silicon using metallo-organic compounds by microwave PECVD systems. The electrical properties of ZrO₂ were studied and results indicated the possible use of the films in microelectronic device fabrication.

References

- Agnihotri O P, Jain S C, Poortmans J, Szlufcik J, Beaucarne G, Nijs J and Mertens R 2000 *Semicond. Sci. Technol.* **15** R29
- Balog M, Schieber M, Michman M and Patai S 1977 *Thin Solid Films* **47** 109

- Cameron M A and George S M 1999 *Thin Solid Films* **348** 90
- Hill W A and Coleman C C 1980 *Solid State Electron.* **23** 987
- Houssa M, Naili M, Zhao C, Bender H, Heyns M M and Stesmans A 2001 *Semicond. Sci. Technol.* **16** 31
- Hubbard D J and Schlom D J 1996 *J. Mater. Res.* **11** 2757
- Kimura S, Murakami E, Miyake K, Warabisako T, Sunami H and Tokuyama T 1985 *J. Electrochem. Soc.* **132** 1460
- Ngai T, Qi W J, Sharma R, Chen X, Lee J C and Banerjee S 2000 *Appl. Phys. Lett.* **76** 502
- Qi W, Nieh R, Lee B H, Kang L, Jeon Y, Onishi K, Ngai T, Banerjee S and Lee J C 1999 *IEDM* 145
- Raoux S, Cheung D, Fodor M, Taylor W N and Fairbairn K 1997 *Plasma Sources Sci. Technol.* **6** 405