Structural and electrical characterization of erbium oxide films grown on Si(100) by low-pressure metalorganic chemical vapor deposition

M. P. Singh, C. S. Thakur, K. Shalini, N. Bhat, and S. A. Shivashankar^{a)}
Indian Institute of Science, Bangalore-560 012, India

We report the structural and electrical properties of Er_2O_3 films grown on Si(100) in the temperature range 450–600 °C by low-pressure metalorganic chemical vapor deposition using $\text{Er}(\text{acac})_3 \cdot \text{phen}$, the phenanthroline adduct of erbium acetylacetonate, as the precursor. The film properties are correlated with the growth and processing conditions. The structural characterization reveals that films grown at lower temperatures are smooth, but poorly crystalline, whereas films grown at higher temperatures are polycrystalline. A dielectric constant in the range 8–20, a minimum total fixed oxide charge density (N_f) of $-1 \times 10^{10} \text{ cm}^{-2}$, and a minimum hysteresis of 10 mV in the bidirectional capacitance–voltage characteristics are demonstrated.

Erbium oxide has several advantages over SiO_2 as a gate dielectric in semiconductor devices. It has a high dielectric constant^{1–5} (10–14), large band gap, and is chemically stable with silicon.³ Hence, Er_2O_3 is currently being studied as a gate dielectric for complementary metal–oxide–semiconductor devices.^{1–4}

Films of Er_2O_3 have usually been prepared by physical vapor deposition techniques, such as thermal evaporation.^{1–4,6} Recently, Ono *et al.*³ have grown Er_2O_3 films on silicon by thermal evaporation of erbium acetylacetonate, a metalorganic complex of erbium, followed by oxidation.

Here, we report the structural and electrical properties of Er_2O_3 films on Si(100) grown by an alternative technique, viz., low-pressure metalorganic chemical vapor deposition (MOCVD), which offers relatively low growth temperatures. Films were deposited at temperatures ranging from 450 to 600 °C and a total pressure of 2 Torr, using 30 sccm of ultra-high-purity (UHP) argon and 100 sccm of UHP oxygen as the carrier and reactant gases, respectively. Films were deposited using $\text{Er}(\text{acac})_3 \cdot \text{phen}$ (99.99%), as the precursor, which was sublimed at 200 °C. Unlike $\text{Er}(\text{acac})_3$, this adduct is stable against oligomerization, which would have resulted in progressively diminishing vapor pressure. Depending on the chemical vapor deposition growth conditions, the film thickness ranged from 100 to 700 nm, as estimated by stylus profilometry, and confirmed by cross-sectional scanning electron microscopy (SEM). Postdeposition annealing (PDA) of the films was carried out for different durations in oxygen at 600 and 700 °C. To fabricate metal–insulator–semiconductor capacitors, aluminum was thermally evaporated onto the $\text{Er}_2\text{O}_3/\text{Si}$ structure, and postmetallization annealing was carried out at 400 °C for 30 min in argon ambient.

The crystal structure of Er_2O_3 is well documented.⁷ In general, it is cubic, with some conditions leading to the hexagonal form. Figure 1 shows the x-ray diffraction [(XRD),

$\text{Cu K}\alpha$ radiation] patterns of the films grown at different temperatures. Films grown at 500 °C show broad, featureless patterns indicating poor crystallinity, whereas those deposited at or above 525 °C show sharp peaks and are polycrystalline. Films deposited at 525 °C show a strong (222) reflection, whereas those deposited at 600 °C exhibit a strong (400) reflection. Apart from the strong (222), (400), and (440) peaks, minor ones are present in the films. Thus, our study shows that the texture of the Er_2O_3 film on silicon is strongly dependent on the growth condition, consistent with the literature.^{1–3} PDA leads to the crystallization of amorphous films, but annealing does not alter the texture of those that are crystalline as deposited. XRD reveals further that PDA results in the removal of the less intense peaks in textured films and in increased grain size. The grain size in the films is in the range 18–35 nm, as estimated using the Debye–Scherrer relation.

Film morphology was examined by atomic force microscopy (AFM) and SEM. Films grown below 525 °C are smooth with a mirror-like reflection sheen, whereas those

FIG. 1. XRD patterns of films grown at (a) 500 °C, (b) 525 °C, and (c) 600 °C.

^{a)}Electronic mail: shivu@mrc.iisc.ernet.in

FIG. 2. AFM micrograph of a film grown at 600 °C (a) as grown and (b) after annealing at 600 °C in O₂ for 20 min.

grown above 525 °C are grainy, as examined by SEM. Figure 2 shows the AFM scan of as-grown and annealed films, revealing that a low-temperature-grown film (525 °C) exhibits a roughness of 2.1 nm, while one grown at a higher temperature (600 °C) has a roughness of 2.6 nm. This increase in roughness can be understood on the basis of grain growth and texture of the films, consistent with XRD. PDA causes surface roughness to develop, due to grain growth. AFM also indicates that films become denser upon annealing.

The presence of heteroatoms in the films (i.e., C and H, deriving from the precursor), and the formation of a silicate at the film–substrate interface, was investigated by Fourier transform infrared (FTIR) spectroscopy in the transmission mode. FTIR spectroscopy reveals (Fig. 3) clearly that the as-grown films are free from heteroatoms and an interfacial silicate layer. This is consistent with the report by Ono *et al.*³ that the possibility of silicate formation at the Er₂O₃/Si interface due to annealing is less than with the other rare-earth oxides. The FTIR spectra further reveal that there is a small amount of O–H present in the film. This is likely due to the absorption of moisture from the atmosphere. The composition of the film grown at 600 °C was also examined by Auger electron spectroscopy, which shows that the Er/O ratio is 1:1.5, and that no carbon is present in the film, except at the top surface, which arises from exposure of the film to atmosphere (Fig. 3).

Room-temperature, high-frequency (1 MHz) capacitance–voltage (*C–V*) measurements were carried out on various films. The effective dielectric constant, which ranges from 8 to 20, was extracted from the accumulation capacitance. Saxena *et al.*⁶ have reported that the dielectric constant of Er₂O₃ films depends strongly on thickness, and may attain a value of 30. Table I summarizes the various parameters extracted from the *C–V* characteristics of the as-grown films. Films grown at lower temperatures have ten times higher N_f than films grown at higher temperatures. Films grown at up to 525 °C have shown larger stretch-out

FIG. 3. (a) AES depth profile and (b) FTIR spectra of an Er₂O₃ film grown at 600 °C.

and hysteresis in bidirectional *C–V* characteristics, whereas films grown above 525 °C have less stretch-out and hysteresis. Stretch-out and counterclockwise hysteresis in bidirectional *C–V* characteristics are indicative of fast and slow interface traps, respectively.

Annealing low-temperature-grown films reduces *C–V* stretch-out and lowers N_f by almost an order of magnitude, while V_{fb} shifts to negative values. For example, PDA of 525 °C grown films at 600 °C for 20 min resulted in $N_f = -1.41 \times 10^{10} \text{ cm}^{-2}$, $V_{fb} = 0.01 \text{ V}$, and hysteresis of 60 mV, whereas PDA at 700 °C for 20 min resulted in $N_f = -6.25 \times 10^{10} \text{ cm}^{-2}$, $V_{fb} = 0.3 \text{ V}$, and hysteresis of 30 mV. Figure 4 shows the bidirectional *C–V* characteristics of the film grown at 525 °C and flash annealed at 700 °C for 30 s in oxygen. Thus, PDA reduces total fixed oxide charge, hysteresis, and stretch-out.

TABLE I. Electrical properties of as-grown films extracted from the *C–V* curve.

Growth temperature (°C)	Hysteresis ΔV (mV)	Flatband voltage V_{fb} (V)	Total fixed oxide charge N_f (cm^{-2})	Stretch-out
500	150	3.89	-2.62×10^{11}	High
525	100	2.19	-3.23×10^{11}	Medium
550	70	0.05	-2.44×10^{10}	Very low
600	60	-0.29	3.0×10^{10}	Very low

FIG. 4. Bidirectional $C-V$ characteristics of a film grown at 525 °C, and flash annealed at 700 °C for 30 s. Thickness of the film is 650 nm and capacitance area= $5.02 \times 10^{-3} \text{ cm}^2$.

Dc current-voltage ($I-V$) measurement was carried out to study the leakage behavior of the films. Figure 5 summarizes the leakage behavior of the as-grown films. The high leakage in the 500 °C film is probably due to the presence of heteroatoms, which leads also to $C-V$ stretchout. The film grown at 550 °C shows a leakage current density (LCD) of $\sim 10^{-4} \text{ A/cm}^2$ at 1 MV/cm, whereas it is 10^{-3} A/cm^2 in the film grown at 525 °C. The LCD increases between films grown at 550 and 600 °C, attributable to increased crystallinity. However, annealing the 525 °C-grown films for 20 min at 600 and 700 °C, respectively, resulted in LCDs of 7.65×10^{-5} and $3.42 \times 10^{-6} \text{ A/cm}^2$. Thus, annealing results in the reduction of the LCD, which is due to densification, as evidenced by AFM.

To summarize, we have synthesized Er_2O_3 films on Si(100) by low-pressure MOCVD using $\text{Er}(\text{acac})_3 \cdot \text{phen}$ as a precursor, and studied their electrical properties. Our study reveals that the properties of the films strongly depend on

FIG. 5. Growth temperature dependence of leakage current density of films at 1 MV/cm.

growth and annealing conditions. FTIR and Auger electron spectroscopy (AES) analyses reveal that films grown at higher temperatures are free of heteroatoms and an interfacial silicate layer. AFM and XRD reveal that the films are smooth (low deposition temperature), and crystalline and textured (high deposition temperature). The annealed films show very good electrical characteristics.

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