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Superior electrical properties of crystalline Er_2O_3 films epitaxially grown on Si substrates

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Crystalline Er_2O_3 thin films were epitaxially grown on Si (001) substrates. The dielectric constant of the film with an equivalent oxide thickness of 2.0 nm is 14.4. The leakage current density as small as 1.6×10^{-4} A/cm^2 at a reversed bias voltage of −1 V has been measured. Atomically sharp Er_2O_3/Si interface, superior electrical properties, and good time stability of the Er_2O_3 thin film indicate that crystalline Er_2O_3 thin film can be an ideal candidate of future electronic devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2208958]

To meet the requirement of International Technology Roadmap for Semiconductors (IRTS), 50 nm complementary metal oxide semiconductor (CMOS) devices must be realized by the end of this decade. Accordingly, the thickness of the commonly used gate SiO_2 layer must be reduced to the level of 0.6–0.8 nm with the scaling down of whole metal oxide semiconductor field effect transistor (MOSFET) devices.[1] However, when the thickness of the oxide layer decreases to 2 nm or less, the tunneling effect becomes significant, resulting in an exceptional increase of the leakage (tunneling) current (up to a level of 10 A/cm^2).[2] In order to reduce such a leakage current, metal oxide layers with high dielectric constants (high k) are required and need to be developed.[3] To convert such a system to a corresponding SiO_2 system, we may define an equivalent oxide thickness (EOT) as

$$\mathrm{EOT} = tk_{\mathrm{SiO2}}/k_m, \tag{1}$$

where t, k_{SiO2}, and k_m are the physical thickness of a high-k oxide layer, the dielectric constant of SiO_2, and the dielectric constant of the high-k oxide layer, respectively. From this equation, it is seen that, for a given physical thickness of an oxide layer (to be sufficiently thick to prevent the leakage current), the EOT is inversely proportional to its dielectric constant. When scaling down MOSFET devices, the EOT needs to be reduced accordingly. To attain a reduced EOT while using a relatively thick oxide layer, the oxide layer must exhibit a high dielectric constant.

Apart from the high dielectric constant, it is generally believed that, for a high-k material, it is essential for it to have a low gate current, good stability (in terms of service time), and a low interface state density. Because of this, the search for suitable oxide layers has been carried out extensively, such as $SrTiO_3$,[4] HfO_2,[5] ZrO_2,[6] and Al_2O_3.[7] Among these materials, HfO_2 has been believed to be a promising high-k oxide in the near future. In general, rare earth (RE) oxides have relatively high dielectric constants, larger band gaps (~5.4 eV),[8] higher conduction band offset with Si (over 2 eV),[9] and a good thermodynamic stability.[10,11] Recently, RE oxide thin films, such as Y_2O_3,[12,13] Pr_2O_3,[14–16] and La_2O_3,[16] have been studied. In this work, we concentrate on the Er_2O_3 oxide thin film. This is because Er_2O_3 thin film is the most stable one of RE oxide thin films, particularly in high temperatures such as 900 °C,[17] which puts it as a unique candidate in high-temperature devices. For this reason, the electrical property of Er_2O_3 films was studied 30 years ago.[18] In recent years, Er_2O_3 thin films grown on Si substrates were achieved in several groups with different techniques.[10,19,20] For example, Mikhelashvili and Eisenstein[10] grew a series of Er_2O_3 thin films with different thicknesses using electron-beam gun evaporation. They measured k_m=9 for a 10 nm thick Er_2O_3 thin film. This low k_m value is due to the nature of its structure—a mixture of amorphous and polycrystalline phases as a result of the deposition technique. To achieve improved electrical properties of Er_2O_3 thin films, we used molecular beam epitaxy (MBE) technique to grow Er_2O_3 thin films with thicknesses less than 10 nm.[20] In this study, the nanostructure of Er_2O_3 thin films and their electrical properties are investigated and the physical reasons behind the demonstrated electrical properties are discussed.

Approximately 7.5 nm thick Er_2O_3 thin film was grown on a 1.5 in., p-type Si (001) wafer with a resistivity of 2–10 Ω cm by MBE with a growth temperature of 700 °C. The details of the growth has been given in our previous publication.[20] After growth, the sample was annealed at 450 °C for 30 min in 1 atm O_2 ambience. The structure of the Er_2O_3 thin film and the interface between the film and its underlying Si substrate were investigated by x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The surface morphologies of the Er_2O_3 thin film was characterized by atomic force microscopy (AFM). Their electrical properties, such as capacitance-voltage (C-V) and current-voltage (I-V) characteristics, were measured by an HP 4284 *LCR* meter and a Keithley 2400 sourcemeter, respectively (in which metallic Al was deposited on both sides of the sample as electrodes).

Figure 1 is an XRD pattern with the diffraction vector along the growth direction and shows only one diffraction peak at 2θ=48.84° that corresponds to the {440} lattice spacing of the cubic Er_2O_3 structure. This indicates that the ⟨110⟩

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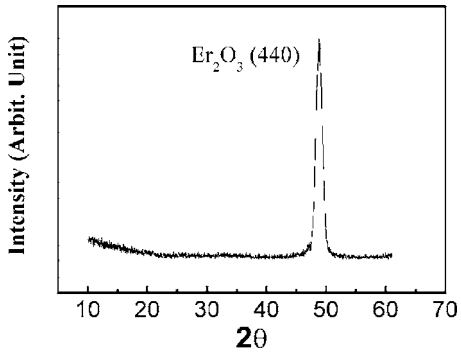

FIG. 1. An XRD pattern of an Er_2O_3 thin film with the diffraction vector along the growth direction.

direction of cubic Er_2O_3 is well aligned with the [001] direction of the Si substrate.

To certify the structure of the Er_2O_3 thin film and the interfacial structure between Er_2O_3 and Si, HRTEM was carried out on cross-sectional specimens. Figure 2 shows a typical HRTEM image, taken along the ⟨110⟩ direction of the Si substrate. From Fig. 2(a), we can see the ripple of the film surface with the maximum thickness of ~8 nm. Figure 2(b) is enlarged image from a part of Fig. 2(a), where it is clearly shown that the Er_2O_3 structure is well aligned with the Si structure. Unlike other promising metal oxide films (such as HfO_2 and Pr_2O_3) where an interfacial layer might be formed between the metal oxide film and the Si substrate, a relatively sharp interface can be clearly revealed. The thin white layer at the interface perhaps represents oxidized silicon.

Figure 3(a) shows high-frequency *C-V* curves of the Er_2O_3 thin film with a MOS structure, measured at 10 kHz. Measurement along the forward direction means the measurement starting from an accumulation region to an inversion region. Based on the capacitance value in the accumulation region, the dielectric constant of the oxide film can be calculated to be 14.4 and, correspondingly, EOT to be 2.0 nm. In Fig. 3, we find that hysteresis in bidirectional *C-V* characteristics is very small, indicating that our oxide film has a very low inner-interface trap density.[21]

It is well known that,[22] for a dielectric material film, the fixed charge density in an oxide film is another issue in real applications, which can be calculated using the following equation:

$$Q/S = C_{ox}(-V_{ms} - V_{FB})/S, \tag{2}$$

where Q is the amount of the fixed charge within the electrode area of the film, S is the electrode area (can be determined by direct measurement), C_{ox} is the capacitance of the oxide layer (in our case, which is equal to the capacitance in the accumulation region of the *C-V* curve), V_{ms} is the difference of the work functions between the semiconductor substrate and the metal gate (for a given material system, V_{ms} is fixed and can be calculated; in our Al/Si system, V_{ms} =0.65 V), and V_{FB} is the flat-band voltage and its value can be extracted from the *C-V* curve with the calculated the flat-band capacitance. Other researchers have reported the value of fixed charge density from 8×10^{13} to 1×10^{10} cm^{-2}.[8,10,19] Based on our measurements, we have obtained that the maximum fixed charge density in our Er_2O_3 thin film is less than 10^{12} cm^{-2}.

Figure 3(b) shows the *I-V* curve of the Er_2O_3 thin film with the MOS structure. Well behaved *I-V* curve is observed.

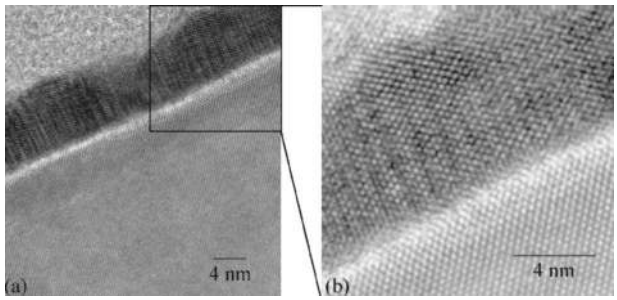

FIG. 2. (a) A typical HRTEM image of an Er_2O_3 thin film grown on a Si (001) substrate and (b) an enlarged HRTEM image of (a).

The leakage current density has been measured to be as small as 1.6×10^{-4} A/cm^2 at a reversed bias voltage of −1 V. With a reversed bias voltage less than 4.5 V, no breakdown is observed.

It is of interest to compare the electrical property of our Er_2O_3 thin film with HfO_2 thin films, the most promising future high-*k* material. Hong *et al.*[23] reported that, for a typical HfO_2 thin film, an EOT=4.3–5.2 nm has a leakage current density of $(2.5–2.7)\times10^{-2}$ A/cm^2 measured at −1.5 V, which is much higher than our case (3.6×10^{-4} A/cm^2 at −1.5 V). In fact, the leakage current density in our case is two orders better than the typical HfO_2 thin film with the comparative EOT thickness, which satisfies commercial applications. It is well known that the leakage current is related to the material energy band alignment and crystal structure.[24] Based on our estimation using x-ray photoelectron spectroscopy (XPS), the band gap of our Er_2O_3 thin film is 7.5 eV and the conduction band offset for our Er_2O_3/Si structure is ~3.5 eV. In contrast, the band gap of HfO_2 thin film has been determined to be 5.8 eV with ~1.5 eV of the conduction band offset for the HfO_2/Si structure.[24] The comparison of these values implies that there is a much higher barrier for electrons in the interface between the Er_2O_3 layer and the Si substrate, which will eliminate the leakage current significantly. The sharp interface observed by HRTEM indicates that the low leakage current is intrinsic of the thin film.

It is worth to notice that annealing in O_2 ambience is a critical process to improve the electrical properties of the Er_2O_3 thin film. In order to estimate the importance of using oxygen as an annealing medium, the electrical properties of the Er_2O_3 thin film annealed in O_2 and N_2 ambiences were measured and compared. It was found that the dielectric constant of the Er_2O_3 film annealed in N_2 ambience is ~70% of the dielectric constant of the Er_2O_3 film annealed in O_2 ambience. This indicates that the as-deposited Er_2O_3 thin film is

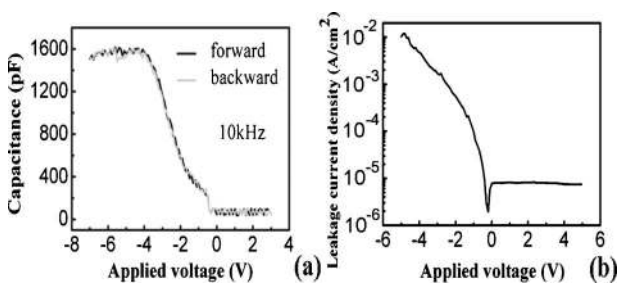

FIG. 3. Electrical properties of the crystalline Er_2O_3 film are shown. (a) *C-V* curves of the Er_2O_3 film tested at 10 kHz. A small hysteresis in bidirectional *C-V* characteristics can be seen. (b) The *I-V* curve of the Er_2O_3 thin film. Leakage current density can be directly measured from this plot.

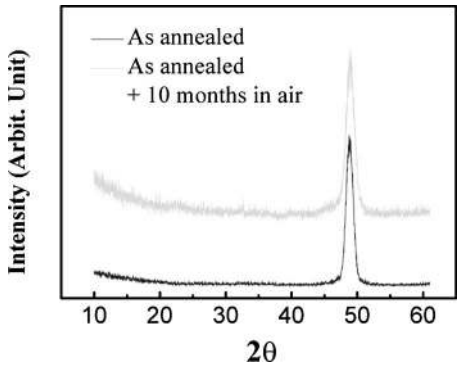

FIG. 4. XRD patterns of the Er_2O_3 thin film taking ten months apart.

deficient in oxygen, and annealing it in O_2 ambience provides oxygen to adjust the film stoichiometric ratio and in turn to improve its electrical properties. AFM results (taken before and after annealing the thin film in O_2 ambience) show that the surface root mean square (rms) changes from 0.75 to 0.36 nm after the annealing process, indicating that a smoother surface can be achieved through the annealing process and the annealing process is critical to improve the electrical properties of the Er_2O_3 thin film.

In order to investigate the stability of the Er_2O_3 thin film under air exposure, XRD patterns of the Er_2O_3 thin film were recorded in a regular interval. Figure 4 shows two XRD patterns taking ten months apart. There is no obvious change in their XRD patterns, implying no structural degradation during this period of time. This is in a strong contrast to the Pr_2O_3 thin film grown on Si,[25] where the structure of Pr_2O_3 thin film has changed even after several days of preparation. The electrical properties of our Er_2O_3 thin film were also frequently measured to assess its stability. Again, the result confirmed that the dielectric properties were not degraded after five months exposure in atmosphere.

In summary, we have grown crystalline Er_2O_3 films on the Si (001) substrate through the epitaxial growth. The measured electrical properties of the thin film suggest that the epitaxially grown Er_2O_3 thin film can be an ideal candidate of future electronic devices, particularly for high-temperature applications. Atomically sharp interface found through HR-TEM in the Er_2O_3/Si interface indicates that the near-perfect epitaxial growth is responsible to the superior electrical properties.

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