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Lanthanide rare earth oxide thin film as an alternative gate oxide



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ABSTRACT

An ultrathin gate oxide is needed for future nanoscale technology due to the density of integrated circuits will increase exponentially every two to three years as predicted by Moore's Law. Some problems were occurred in conventional silicon dioxide gate oxide during applications such as high leakage current density, low reliability issues, and undesirable power dissipation. Lanthanide rare earth oxides was attracted as one of potential candidates to replace conventional silicon dioxide due to their superior properties. Each rare earth oxides in lanthanide group was reviewed and discussed in terms of physical, chemical, and electrical properties and also its common deposition methods. Sm₂O₃ is one of the promising candidate materials among rare earth oxides because of some outstanding properties such as high κ (7–22), high breakdown electric field (5–7 MV cm⁻¹), relatively large bandgap (4.33 eV), low leakage current, large conduction offset with Si, high thermal stability, small frequency dispersion, low trapping rate, and low hygroscopic characteristic. The literatures of Sm₂O₃ was paid particular attention in the last section. The previous deposition methods of the Sm₂O₃ as gate oxide were reviewed and compared.

1. Introduction

As predicted by Moore's Law, the density of integrated circuit and the number of devices will increase exponentially and double every two to three years [1-6]. This significant development of technology requires ultrathin gate oxide (~ 1.5 nm or 4 atomic layers) of silicon dioxide (SiO₂) layer [1,3,7,8]. An extremely thin film may lead to large leakage current density owing to large amount of quantum-mechanical tunneling through the gate oxide and low reliability of gate oxide against the electrical breakdown [1,3,7]. This may cause unacceptable static power dissipation in the device [1,3,9]. The gate leakage problem occurred since late 1990s [2,3,10,11]. However, this problem is not solved completely even though enormous ingenuity and efforts were done by numerous researchers due to continued downscaling trend. For CMOS technology, a specific gate capacitance was designed to be proportional to the dielectric constant (κ) and inversely proportional to the thickness of the gate oxide [1,12]. For the sake of reducing leakage current density, a thicker film with high κ must be introduced to replace conventional SiO₂.

Based on previous research works, actually many studies have been done to replace SiO₂ layer as gate oxide such as HfO₂ [12–15], ZrO₂ [12,13,16–19], ZrON [19–24], Al₂O₃ [25–28], TiO₂ [1,9,12,16], Ta₂O₅ [1,9,12,16], and Y₂O₃ [29–35]. Unfortunately, each of them has their own limitations and drawbacks compared to SiO₂ layers. For HfO₂ and ZrO₂, six problems have been summarized in Chin et al. review paper

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[36]. There are (1) interfacial layer formation and growth during deposition and postdeposition annealing, (2) growth of microcrystal after heat treatment, (3) lateral oxidation at the gate edge, (4) existence of fixed charges, which causes flatband voltage shift, (5) higher interface states density, and (6) contamination of the dielectric from the precursors of chemical vapour deposited dielectric [36–39]. Large fixed charge and interface trap density are obtained in Al₂O₃ [40,41]. TiO₂ and Ta₂O₅ have too low conduction band offsets with Si conduction band and thermodynamic stability [42–44]. TiO₂ and Y₂O₃ are reported to have low crystallization temperature (< 400 °C) [45], which is unflavored in most of the processing temperatures of present MOS fabrication technology. Besides that, the interface density of Y₂O₃ (10¹² eV⁻¹ cm⁻²) is too high for MOS device applications [46].

In this paper, the first section begins by discussing the lanthanide rare earth oxide (REO) as alternative gate oxide. After that, the common deposition methods included PVD and CVD were discussed. Following that, the deposition methods of each lanthanide REO and their performances as gate oxide were reviewed and enumerated. The next section pays particular attention to the literatures of the Sm_2O_3 . Then, the previous deposition methods of the Sm_2O_3 as gate oxide were reviewed and compared. Lastly, the challenges to be overcome in the future are also reported in this review.

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Fig. 1. The interrelationship between dielectric constant and bandgap of lanthanide REOs [36]. The black dots represented those oxides with higher dielectric constant (> 12) and larger bandgap (\geq 5 eV).

2. Lanthanide rare earth oxide (REO) as alternative gate oxide

Recently, the lanthanide rare earth oxides (REOs) (Fig. 1) have been investigated due to some superior properties such as high dielectric constant, relatively large bandgap, high breakdown electric field, high resistivity, high conduction offset, low interface trap density, smooth surface, small lattice mismatch with silicon, and high thermal and chemical stability. REOs have been widely used in electronic devices such as, frequencies switches, reprogrammable memory circuits, capacitors, transistors, and varicaps [47–59]. The deposition methods, thickness, and electrical performances of lanthanide REOs films were summarized in Table 1.

The lanthanide REOs have higher dielectric constant (κ = between 7 and 30) than SiO₂ (κ = 3.9). High dielectric constant allows reducing equivalent oxide thickness (*EOT*) for downscaling purposes [54,60]. Higher dielectric constant can avoid using ultrathin thickness of gate oxides which may lead to undesirable current leakage due to direct tunneling of electron through gate oxides [61]. A high enough bandgap is also required for insulating properties. Normally, the bandgap should be higher than 5 eV. Only five of these lanthanide REOs are higher than 5 eV which is prior consideration as replacement candidate as shown in Fig. 2 [36].

REOs are predicted to be chemically or thermodynamically stable when in contact with Si substrates because they able to resist silicide formation after depositions. The oxygen tends to dissociate easily in air or oxygen during post deposition annealing. This will form SiO_x interfacial layers or rare earth silicates layers. Undesirable interfacial layers may degrade the electric properties due to a reduced κ value. Thus, optimization of deposition parameters of gate oxides is required to minimize formation of interfacial layers [36,54,55,62,63].

Another concern of REOs is the hygroscopic property [62,63]. Hydride, Ln_2O_3 -H₂O will be formed after moisture absorption which may lead to form hydroxide, $Ln(OH)_3$. Undesirable hydroxide may increase film thickness and reduce the dielectric constant value. The hygroscopic property may roughen the surface of gate dielectric and increase leakage current density. The moisture reactivity of REOs is increasing as lattice energy, ionic radius and cations electronegativity of REOs are decreasing. Thus, La_2O_3 is the most hygroscopic (lowest electronegativity and highest lattice energy) while Lu_2O_3 is the least hygroscopic (highest electronegativity and lowest lattice energy) as shown in Fig. 3 [36,53,61,62].

3. Common deposition methods of lanthanide rare earth oxide (REO)

Many deposition methods (Table 1) have been developed for REOs thin films but they can be divided into two main and broad categories.

The first one is chemical vapour deposition (CVD) such as metal organic-CVD (MOCVD), and atomic layer deposition (ALD), while second one is physical vapour deposition (PVD) such as sputtering (radio frequency (RF) and direct current (DC)), vacuum evaporation, thermal evaporation, electron beam evaporation, and pulsed laser deposition (PLD) [9,12,36,64,65].

3.1. Chemical vapour deposition (CVD)

The MOCVD applies basic principles of both CVD and ALD processes. The main difference between them is that MOCVD uses a metalorganic compound as precursor during deposition process [12]. A liquid precursor is advantageous to avoid or limit particle formations [9]. ALD is also known as atomic layer chemical vapour deposition (ALCVD) or atomic layer epitaxy (ALE) [12]. ALD is a thin film deposition process which involved the chemical gas phases and two precursors are deposited and oxidized alternatively in a sequential manner at substrates, called surface controlled growth cycles. The first precursor is introduced in excess and a monolayer of reactant is chemisorbed onto the surface. Then, the first precursor is removed by inert gas before the second precursor is introduced. The second precursor is reacted with the reactant on the surface and produce the desired film. Lastly, the second precursor is removed by inert gas again and the process is completed [36,65,66]. The precursor must be volatile, high purity, nontoxic, no gas phase reactions, no self-decomposition, and no etching of the existing oxide [2,65]. Good film quality, electrical properties, and low contaminations of films can be produced by thermal and plasma enhanced ALD [67]. Both MOCVD and ALD able to control the film thickness precisely with good uniformity and conformal coverage over complex shapes owing to the self-limiting growth mechanism of the precursors [2,9,12,36,65,66].

The chemical deposition methods are more widely used because of the advantages as mentioned in section before such as large area depositions, uniform film, good composition control, high film density, and deposition rates [9,47,64,65]. However, there still have some concerns in chemical depositions such molecular precursor availability, precursor stability, and volatility. High deposition temperatures and/or post deposition annealing are required to decompose metal organic precursors. Thus, large amounts of carbon may present which are detrimental to the electrical properties of the films [2,9,64,68]. As Wong and Chong summarized [12], ALD process has three main limitations: (1) too fine size of particles are difficult to transport from source to the film, (2) poor nucleation on hydrogen terminated silicon, and (3) residue contaminations. A typical example is the carbon content was left in Nd₂O₃ film which deposited by ALD process [68].

3.2. Physical vapour deposition (PVD)

For physical depositions, PLD requires a large energy density of laser beam to ablate the target source and vapourized the materials that eventually sublimate on the substrates [12]. PLD is a clean and simple method to obtain a wide range of structures, compositions, and properties [51]. In electron beam evaporation, an electron beam is used as power source to heat the target source to produce vapourized materials that condensed on substrates in high vacuum ambient [12]. Electron beam evaporation can produce ultrathin and smooth films with excellent electrical properties [12,48,69]. Dense and compact films with low stress can be deposited by electron beam evaporations [70]. The substrates suffer little damage since the electron beam sputters on the target source but not the substrates. However, it is not suitable as a conventional production method.

Sputtering is a process which source materials are ejected from the target source and deposited on the substrate in vacuum chamber [12,36]. DC and RF sputtering are the most common types of sputtering process. DC sputtering is used for target materials with good electrical conductivity while RF sputtering is used for target materials with low

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