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Characterization of gadolinium and lanthanum oxide films on Si (100)

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High-resolution transmission electron microscopy, electron energy loss spectroscopy, and Auger electron spectroscopy, were used to study gadolinium and lanthanum oxide films deposited on Si (100) substrates using electron-beam evaporation from pressed-powder targets. As-deposited films consist of a crystalline oxide layer and an amorphous interfacial layer. A complicated distinct multilayer structure consisting of oxide layers, silicate layers, and SiO₂-rich layers in thick (~30 nm) annealed films has been observed for both gadolinium and lanthanum films. For thinner annealed films (~8 nm), there is no longer a crystalline oxide layer but an amorphous gadolinium or lanthanum silicate layer and an interfacial SiO₂-rich layer. The formation of the lanthanum silicate by annealing lanthanum oxide is found to be thermodynamically more favorable than the formation of gadolinium silicate. © 2002 American Vacuum Society. [DOI: 10.1116/1.1463079]

I. INTRODUCTION

The search continues for high dielectric constant (high- κ) gate dielectrics to replace silicon dioxide in deep submicron complementary metal-oxide-semiconductor (CMOS) technology. The possible candidates include various oxides such as Gd₂O₃, La₂O₃, Y₂O₃, TiO₂, ZrO₂, and HfO₂.¹ Although thermodynamic calculations have led to the conclusion that these oxides should not react directly with silicon substrates to form a SiO₂ interfacial layer,² in practice it is difficult to avoid the formation of an interfacial oxide layer during deposition and postannealing. Moreover, these oxides tend to crystallize at low temperatures,³ which could result in high conductivity paths along grain boundaries. The formation of a low- κ SiO₂ interfacial layer under a polycrystalline oxide film during the high- κ oxide film deposition and annealing limit the benefits of the high- κ oxide dielectric. Understanding the mechanisms that create the interfacial layers has become one of the main challenges if these high- κ dielectrics are to be an alternative to SiO₂.

Recent efforts have focused on various silicates such as (ZrO₂)_x(SiO₂)_{1-x}, (HfO₂)_x(SiO₂)_{1-x}, and (Gd₂O₃)_x(SiO₂)_{1-x}.^{4,5} The silicate films, which remain amorphous at relatively high temperature, might provide a better interface with Si than the metal-oxide and show the most promise for successful integration into future CMOS technologies. In this article, we report the physical and chemical characterization of gadolinium and lanthanum oxide films on Si (100) and describe the formation of lanthanum and gadolinium silicates by annealing these oxide films.

II. EXPERIMENT

Gd₂O₃ and La₂O₃ films were deposited by electron-beam evaporation of pressed-powder (Gd₂O₃ or La₂O₃) targets onto Si (100) substrates previously cleaned using a RCA HF

last process. Details of the deposition procedures are described elsewhere.⁶ The wafers were cut into pieces after deposition and annealed in a Heatpulse 610 (Steag RTP Systems) rapid thermal processing system in flowing O₂ at 900 °C for 2 min. <011> cross-section transmission electron microscopy (TEM) samples were prepared following standard procedures and examined in a Philips EM430T operating at 250 kV and a Philips CM20 equipped with field emission gun and an energy loss imaging filter (Gatan model 678). Auger electron spectroscopy analysis was performed using a Physical Electronics Industries (PHI) 650 instrument equipped with a 5 keV electron beam 30° off normal. The Si *KLL*, O *KLL*, La *MNN*, and the Gd *NOO* line at 138 eV were used in the derivative mode. An argon ion gun operating at 1 keV, 51° off normal, was used for depth profiling. To calibrate the Auger measurements, Rutherford backscattering (Gd, La, and Si) and nuclear reaction analysis (O) measurements were performed on standard samples using techniques described previously.⁶

III. RESULTS AND DISCUSSION

High-resolution TEM (HRTEM) studies of a 37 nm thick Gd₂O₃ film (sample 1090) revealed the same structures shown in the previous studies of Gd₂O₃ films.⁶⁻⁸ For the as-deposited film, there is a crystalline gadolinium oxide layer and a thin amorphous silicate interfacial layer with a negligible interface oxide layer of <5 Å in thickness. Three layers were observed in the annealed film: Gd₂O₃, (Gd₂O₃)_x(SiO₂)_{1-x}, and SiO₂, respectively.

A thinner as-deposited Gd₂O₃ film (8.5 nm thick, sample 1096) shows a structure similar to the 37 nm thick sample: a crystalline gadolinium oxide layer and a thin amorphous silicate interfacial layer. However, the structure of the annealed film is different. Figure 1(a) is a HRTEM image of the 8.5 nm thick Gd₂O₃ film after annealing at 900 °C in oxygen for 2 min. Instead of three layers in the film, only two layers are

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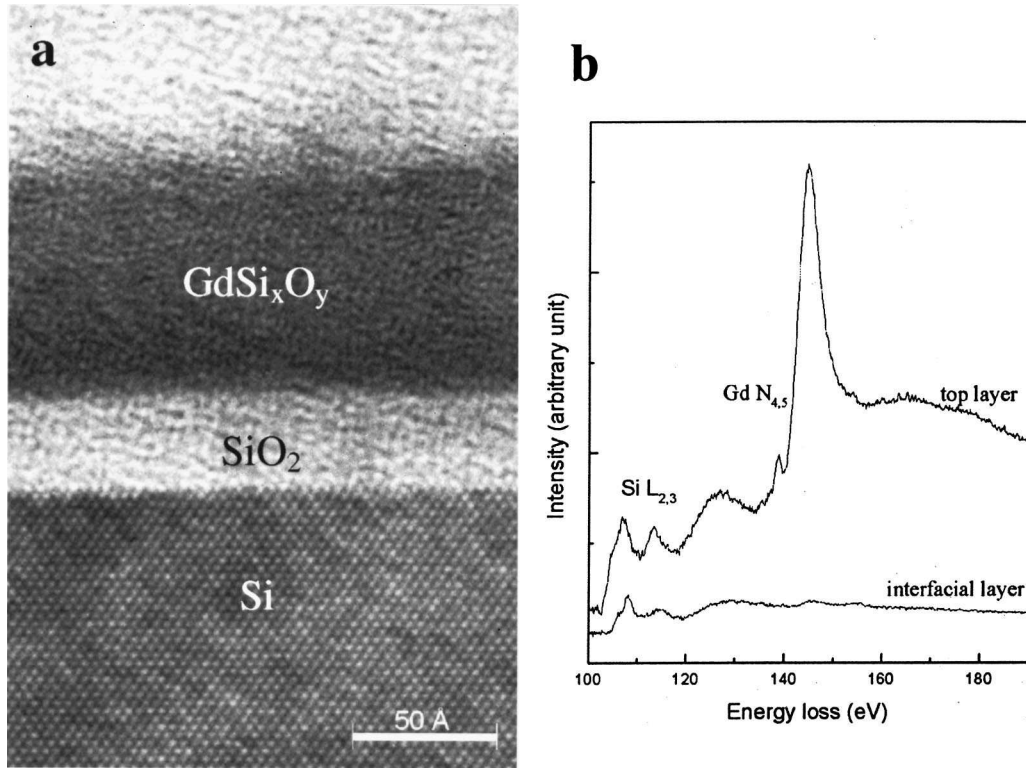


FIG. 1. HRTEM image of an 8.5 nm thick gadolinium oxide film (sample 1096) after being annealed at 900 °C in oxygen for 2 min (a) and corresponding EELS Si $L_{2,3}$ edges and Gd $N_{4,5}$ edges (b).

visible: a 8.5 nm thick dark-contrast amorphous layer and a 3.2 nm thick bright-contrast amorphous interfacial layer. From the thicker film observation, we can conclude that the top dark-contrast amorphous layer is gadolinium silicate $(Gd_2O_3)_x(SiO_2)_{1-x}$, and the bright-contrast amorphous interfacial layer is SiO_2 . Support for this conclusion comes from electron energy loss spectroscopy (EELS) analysis of this film. Figure 1(b) shows Si $L_{2,3}$ edges and Gd $N_{4,5}$ edges recorded from the two layers exhibiting the bright and dark contrast in the HRTEM image of Fig. 1(a). Both Si and Gd were detected in the top dark-contrast amorphous layer, while only Si was detected in the bright-contrast interfacial layer. As expected, this EELS result confirms the conclusion that the top dark-contrast amorphous layer is gadolinium silicate $(Gd_2O_3)_x(SiO_2)_{1-x}$, and the bright-contrast amorphous interfacial layer is SiO_2 . There is no longer a gadolinium oxide layer in the film.

A 32.6 nm thick as-deposited La_2O_3 film (sample 1108) shows a similar structure to the thick as-deposited Gd_2O_3 film: a 3.6 nm thick amorphous layer and a 25 nm thick polycrystalline layer without an oxide interfacial layer [only part of the crystalline layer is shown in Fig. 2(a)]. However, a more complicated structure was found for the sample annealed for 2 min at 900 °C in oxygen [Fig. 2(b)]. Four distinct layers can be seen in the film. They are [from top to bottom in Fig. 2(b)]: a 6.0 nm thick crystalline layer, another crystalline layer of 15.3 nm thick, a 3.0 nm thick dark-contrast amorphous layer, and another 3.3 nm thick lighter-contrast amorphous interfacial layer. It is noted that none of

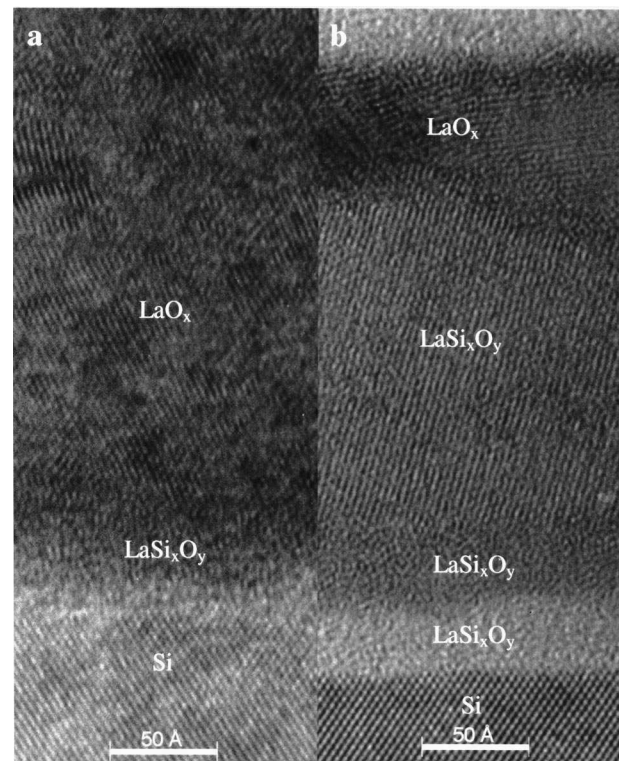


FIG. 2. HRTEM images of a 32.6 nm thick lanthanum oxide film (sample 1108): (a) as-deposited and (b) annealed at 900 °C in oxygen for 2 min.

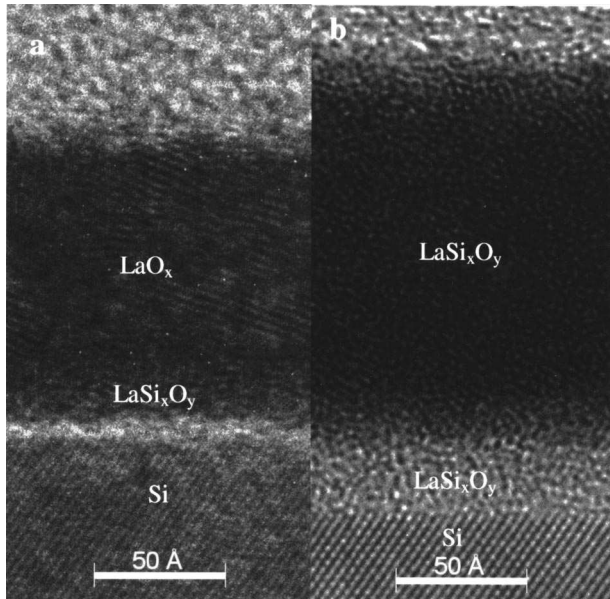


FIG. 3. HRTEM images of a 11.3 nm thick lanthanum oxide film (sample 1106): (a) as-deposited and (b) annealed at 900 °C in oxygen for 2 min.

these layers exhibit the bright contrast of the pure SiO_2 layer as shown in the gadolinium films [Fig. 1(a)].

The formation of lanthanum silicate films by annealing a lanthanum oxide film has also been observed in a thinner film. Figure 3(a) is a HRTEM image of a 11.3 nm thick, as-deposited La_2O_3 film (sample 1106). The film contains a single crystalline lanthanum oxide layer and a negligible interfacial oxide layer of $<5 \text{ \AA}$ in thickness, which is similar to the as-deposited gadolinium oxide film. A two layer structure appears in the film after annealing in oxygen at 900 °C for 2 min: a 14.8 nm thick dark-contrast amorphous layer and a 2.9 nm thick lighter-contrast amorphous interfacial layer [Fig. 3(b)]. After annealing, the crystalline oxide layer became an amorphous silicate layer, and a new interfacial layer was formed. Again, the contrast of the interfacial amorphous layer is different from the bright contrast of the pure SiO_2 layer shown in Fig. 1(a).

The nature and composition of the films were also studied using Auger depth profiling. The results of a 37 nm thick Gd_2O_3 film (sample 1090) [Fig. 4(a)] again are identical to previous observations.^{6,7} The composition is stoichiometric Gd_2O_3 and the three layer structure observed by HRTEM in the annealed film is evident [Fig. 4(a)]. In contrast to the stoichiometric Gd_2O_3 film, lanthanum oxide films are oxygen rich as shown in the Auger depth profiles for two different thickness lanthanum oxide films [Figs. 4(b) and 4(c)]. For a 32.6 nm thick film (sample 1108), the most interesting observation about the Auger depth profile of the annealed La_2O_3 film is that Si is present in all layers but the 6.0 nm top surface layer. Combining the results of HRTEM (Fig. 2) and Auger depth profiles [Fig. 4(b)] for sample 1108, we can conclude that only the top 6 nm surface crystalline layer is the lanthanum oxide layer remaining after annealing.

Figure 4(c) shows Auger depth profiles of the thinner lan-

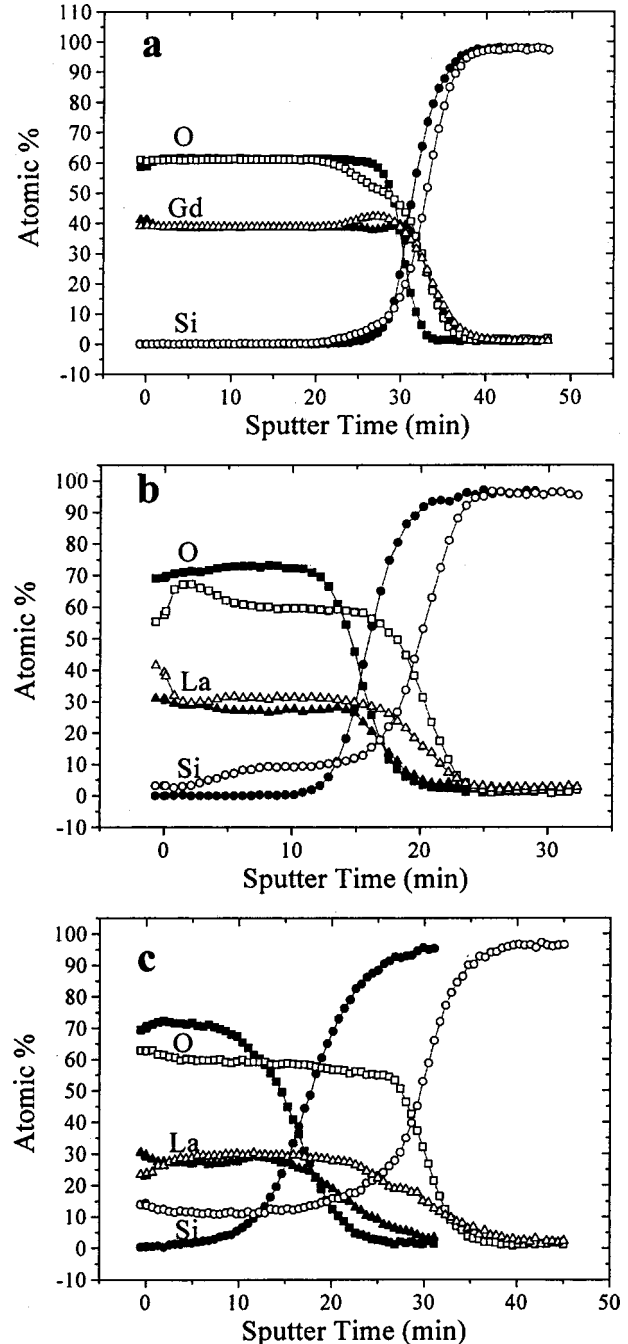


FIG. 4. Auger depth profiles of a 37 nm thick gadolinium film (sample 1090) (a), a 32.6 nm thick lanthanum oxide film (sample 1108) (b), and a 11.3 nm thick lanthanum oxide film (sample 1106) (c). Solid symbols are for as-deposited film and open symbols for the films annealed at 900 °C in oxygen for 2 min.

thanum oxide film (11.3 nm thick, sample 1106). Si is present in all layers after annealing, which means that there is no lanthanum oxide layer at all in the annealed film. The as-deposited crystalline lanthanum oxide layer has become an amorphous lanthanum silicate layer after annealing as shown in Fig. 3.

We have shown that both gadolinium and lanthanum silicate layers could be formed by annealing gadolinium and lanthanum oxides in oxygen. However, the rate of the forma-

tion of the silicates is different for gadolinium and lanthanum. Comparing the 37 nm thick gadolinium oxide film (sample 1090) and the 32.6 nm thick lanthanum oxide film (sample 1108), we found the formation of lanthanum silicate is easier than the formation of gadolinium silicate. Also, it was found that the maximum oxide thickness that could be completely transformed into silicate by the same annealing condition is smaller for gadolinium oxide than for lanthanum oxide, which again implies that it is easier to form lanthanum silicates. A recent study on interfacial reactions between rare-earth-metal oxide films and Si substrates⁹ has concluded that in rare-earth oxides with large ionic radii, Si atoms from the substrate diffuse easily into the space in the M_2O_3 (M are rare-earth elements) film and form Si-O-M bonds, creating an interfacial MSi_xO_y layer. Since the ionic radius of rare-earth elements decreases with increasing atomic number, the formation of lanthanum silicates is more favorable than the formation of gadolinium silicates. An alternate explanation can be deduced from thermodynamic arguments. Liang *et al.*¹⁰ have derived a relationship for the enthalpy ΔH_f (in kJ/mole) of formation of silicates from silicon dioxide and the corresponding metal oxide, $\Delta H_f = -100.8 + 16.8(z/r)$, where z/r is the ionic potential, z ($=3$) is the ionic charge, and r is the ionic radius in Å. This gives $\Delta H_f = -59.5$ kJ/mole for the formation of La_2SiO_5 and $\Delta H_f = -55.4$ kJ/mole for the formation of Gd_2SiO_5 . Analogous relationships should exist for the formation of the other silicate phases and amorphous silicates from the metal oxides and SiO_2 . With a larger negative enthalpy of formation the lanthanum silicates should form more readily than the gadolinium silicates. All that is required for the silicate-forming reactions to proceed is silicon dioxide and this can be produced at the interface by the reaction between the Si substrate and inward oxygen diffusing from the ambient, either during deposition or postdeposition oxygen annealing. Another study on the structure and stability of La_2O_3/SiO_2 layers on Si (100) has shown that rapid thermal annealing at 800 °C did cause La diffusion into the SiO_2 .¹¹

The formation of rare-earth silicates by annealing the oxides in oxygen also depends strongly on the annealing temperature. If a 7.5 nm gadolinium oxide layer is annealed at 780 °C for 10 min, a multilayer structure with a gadolinium oxide top layer appears.⁷ However, this study shows that for a 8.5 nm thick gadolinium oxide layer annealed at 900 °C for 2 min, the top layer of the film is gadolinium silicate and there is no longer a gadolinium oxide layer present in the film (Fig. 2). Higher temperature speeds up the diffusion of Si from the substrate.

There is a SiO_2 -rich interfacial layer right above the Si substrate after rare-earth oxides are annealed in oxygen as shown in the HRTEM images. The thickness of this interfacial layer decreases slightly with an increase in the original oxide layer thickness for both gadolinium and lanthanum. We can conclude that the Si substrate reacted with oxygen mainly diffused from the annealing atmosphere through the oxide layer to form the SiO_2 layer. The thicker the oxide layer, the more difficult for the oxygen to diffuse, which

results in a decreased thickness of this interfacial layer. There is a difference in this interfacial layer for gadolinium and lanthanum films: for gadolinium films, this interfacial layer is pure SiO_2 , while the layer is a SiO_2 -rich silicate for the lanthanum films. This low- κ SiO_2 rich interfacial layer sets a limit on the minimum achievable equivalent oxide thickness, and thus should be avoided. Since this SiO_2 -rich interfacial layer is formed by the reaction between the Si substrate and oxygen mainly from the annealing atmosphere, the thickness of this layer could be reduced if the samples were annealed in an oxygen-free environment. It should be noted that unlike similar films in a CMOS process, the films in this study were annealed in an "uncapped" state, i.e., the oxide is exposed during the annealing, which could result in more oxygen diffusing to the interface. Also, the hygroscopic nature of these films,¹² especially La-based films, could have some impact on the formation of the interfacial SiO_2 -rich layer. We would expect the thickness of this SiO_2 -rich layer to be less if the Gd- and La-based films were "capped."

IV. CONCLUSIONS

Both gadolinium and lanthanum silicate as-deposited films have a similar structure: a crystalline oxide layer and a thin amorphous silicate interfacial layer. After annealing in oxygen at 900 °C for 2 min, thick gadolinium and lanthanum films have a complicated distinct multilayer structure consisting of oxide layers, silicate layers, and SiO_2 -rich layers. For thinner annealed films, there is no longer a crystalline oxide layer but an amorphous gadolinium or lanthanum silicate layer and an interfacial SiO_2 -rich layer in the films. The formation of the lanthanum silicate by annealing lanthanum oxide is found to be thermodynamically more favorable than the formation of gadolinium silicate.

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