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Structural comparison of gadolinium and lanthanum silicate films on Si(1 0 0) by HRTEM, EELS and SAED

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Abstract

High-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) were used to study gadolinium and lanthanum silicate films deposited on Si(1 0 0) substrates using electron-beam evaporation from pressed-powder targets. As-deposited films consist of an amorphous silicate layer without an interfacial layer. After annealing at 900 °C in oxygen for 2 min, an interfacial SiO_2 layer is formed in the gadolinium silicate film, while this interfacial layer is a SiO_2-rich lanthanum silicate layer in the lanthanum silicate film. The formation of interfacial silicate layers is thermodynamically more favorable for the lanthanum films than for the gadolinium films. The gadolinium silicate films crystallize at a temperature between 1000 and 1050 °C, while the crystallization temperature for the lanthanum silicate films is between 900 and 950 °C.
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1. Introduction

Replacing silicon dioxide with high dielectric constant (high-κ) materials systems as the gate dielectrics in deep submicron complementary metal oxide semiconductor (CMOS) technology has drawn increased attention in recent years. Among the possible candidates, various oxides such as Gd_2O_3, La_2O_3, Y_2O_3, ZrO_2 and HfO_2 stand out because of their high dielectric constants [1]. Although thermodynamic calculations indicate that these oxides should not react directly with silicon substrates to form a SiO_2 interfacial layer [2], in practice it is difficult to avoid the formation of an interfacial oxide layer during deposition and post-annealing. 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 SiO_2 interfacial layer under a polycrystalline oxide film during the high-κ oxide film deposition and annealing limits the benefits of the high-κ oxide dielectric.

Recent efforts have focused on various so-called pseudobinary materials systems such as $(ZrO_2)_x(SiO_2)_{1-x}$, $(HfO_2)_x(SiO_2)_{1-x}$ and $(Gd_2O_3)_x(SiO_2)_{1-x}$ [4,5]. These silicate films have advantages over pure metal oxides since they have higher crystallization temperatures

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allowing them to remain amorphous during high-temperature processing. The silicates might provide a better interface with Si than the metal oxide, and they may also be less susceptible to B, Si or O diffusion. Moreover, the use of pseudobinary materials systems provides a large flexibility in selecting the film composition to tailor the electrical properties. These silicates show the most promise for successful integration into future CMOS technologies. In this work, we present the structural characterization of gadolinium and lanthanum silicate films on Si(1 0 0) by high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED).

2. Experimental procedures

A gadolinium silicate film and a lanthanum silicate film were deposited by electron-beam evaporation of mixed $(SiO_2)_{0.33}(M_2O_3)_{0.67}$ (M = Gd or La) pressed-powder targets onto Si(1 0 0) substrates previously cleaned using a RCA HF last process. The details of the deposition procedures are described elsewhere [6]. Both the gadolinium and lanthanum silicate films have similar compositions, determined to be $M_{0.23}Si_{0.14}O_{0.63}$ (i.e. 55% SiO_2 + 45% M_2O_3) using Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA) techniques. The wafers were cut into pieces after deposition and annealed in a Heatpulse 610 (Steag RTP Systems) rapid thermal processing system in flowing O_2 at 900 °C for 2 min, <0 1 1> 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 field emission source TEM with an energy loss imaging filter (Gatan model 678).

3. Results and discussion

Fig. 1 shows HRTEM images of a 30 nm thick gadolinium silicate film as-deposited (Fig. 1a), annealed at 900 °C in oxygen for 2 min (Fig. 1b), and annealed at 1050 °C in oxygen for 15 s (Fig. 1c), respectively. The {0 1 1} plane lattice images of the Si substrate in HRTEM micrographs were used as a

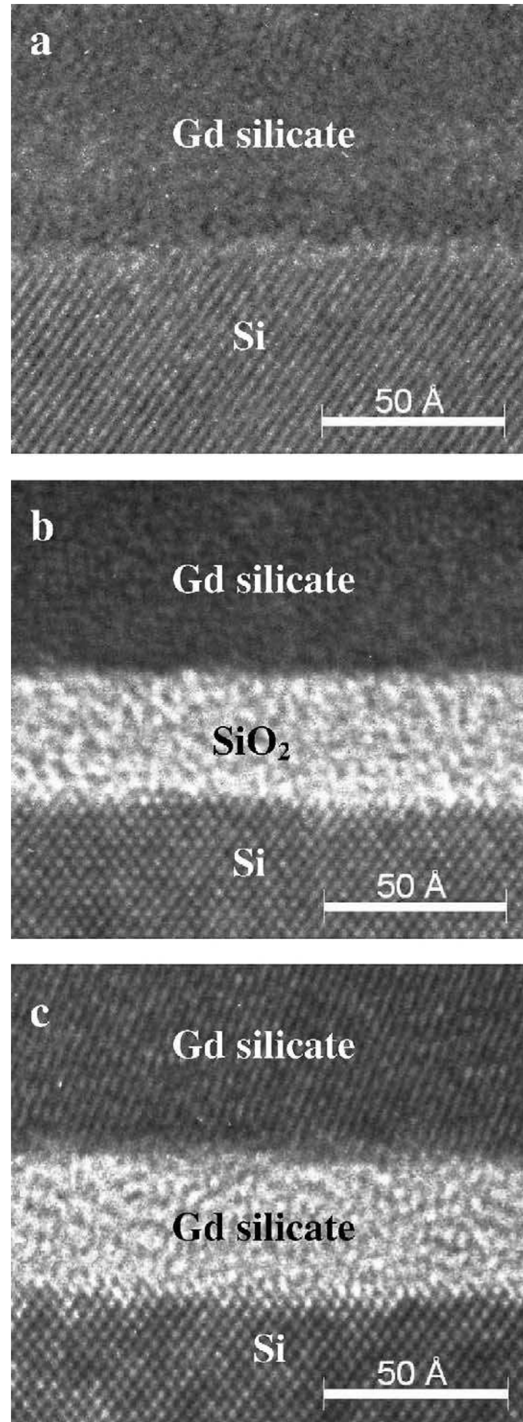


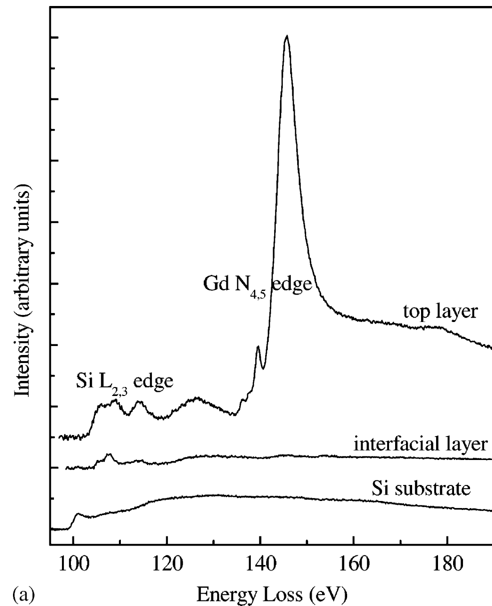
Fig. 1. HRTEM images of a 30 nm thick gadolinium silicate film: (a) as-deposited; (b) annealed at 900 °C in oxygen for 2 min; and (c) annealed at 1050 °C in oxygen for 15 s.

reference to calibrate the magnification, and measure the film thickness. For the as-deposited film, there is a 30 nm thick amorphous silicate layer (only part of this amorphous layer is shown in (Fig. 1a) without an interfacial layer. On the other hand, an interfacial layer is observed in the annealed films (Fig. 1b and c). After annealing at 900 °C, there is a 3.4 nm thick bright-contrast interfacial layer between the silicon substrate and the amorphous silicate layer (Fig. 1b). A similar structure is observed for the sample annealed at 1050 °C, but the top silicate layer has crystallized (Fig. 1c).

EELS analysis was performed on the annealed films. Fig. 2a shows the Si $L_{2,3}$ edges and Gd $N_{4,5}$ edges recorded from the top amorphous layer, interfacial layer and Si substrate of the sample annealed at 900 °C. Both Si and Gd were detected in the top amorphous silicate layer as expected. For the interfacial layer, only Si was detected, which means there is no evidence of Gd and this region is pure silicon oxide. O K edges were also obtained from the top amorphous layer and interfacial layer of this sample as shown in Fig. 2b. The fine structures of the O K edges from the top amorphous layer and interfacial layer show typical pure SiO_2 and gadolinium silicate characteristics respectively [7]. Thus, it has been shown that a 3.4 nm thick pure SiO_2 interfacial layer is formed and the gadolinium silicate layer remains amorphous during the rapid thermal annealing at 900 °C. The formation of SiO_2 is likely the result of oxygen from the annealing atmosphere diffusing into the interfacial region through the gadolinium silicate layer and reacting with the silicon to form SiO_2. Oxygen diffusion through the gadolinium silicate film has been assessed by Rutherford backscattering and narrow resonance nuclear profiling and reported elsewhere [8].

The Si $L_{2,3}$ and Gd $N_{4,5}$ edges of the sample annealed at 1050 °C are shown in Fig. 3. In contrast to the sample annealed at 900 °C, a very small amount of Gd was detected in the interfacial layer in this sample indicating that rapid thermal annealing at 1050 °C did cause some diffusion of Gd into the SiO_2 layer.

It was also shown in the Fig. 1c that the gadolinium silicate film annealed at 1050 °C was crystallized, which means that the crystallization temperature is below 1050 °C. To determine the crystallization temperature of the gadolinium silicate films, films were annealed at various temperatures of 850, 900, 950, 1000 and 1050 °C. HRTEM studies of these films revealed that the gadolinium silicate films crystallize



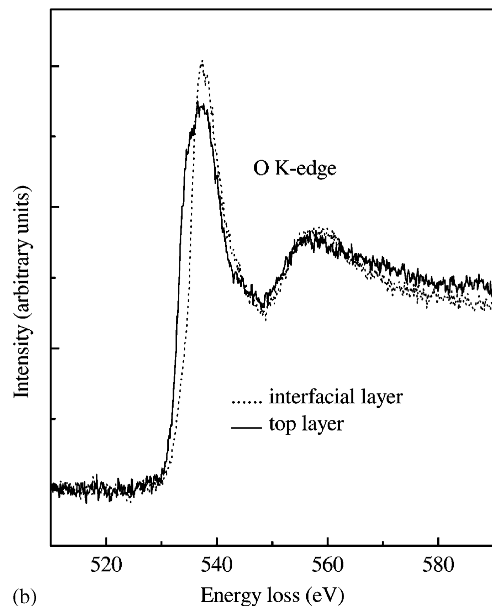


Fig. 2. EELS Si $L_{2,3}$ edges and Gd $N_{4,5}$ edges (a) and O K edges (b) of the gadolinium silicate film after annealing at 900 °C in oxygen for 2 min.

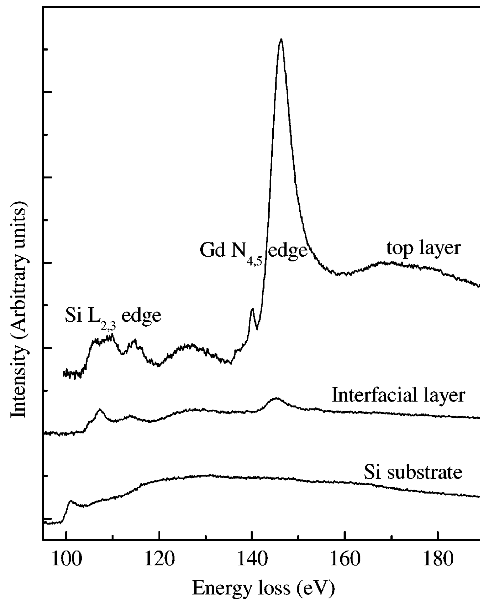


Fig. 3. EELS Si $L_{2,3}$ edges and Gd $N_{4,5}$ edges of the gadolinium silicate film after annealing at 1050 °C in oxygen for 15 s.

at a temperature between 1000 and 1050 °C. To confirm the HRTEM observations, SAED studies were performed on the samples annealed at 1000 and 1050 °C. Fig. 4a shows the SAED pattern taken from the gadolinium silicate layer of the sample annealed at 1000 °C. A discontinuous ring consisting of some distinguishable spots suggests that the film has started to crystallize and some nano-scale crystal clusters have been formed at this temperature. Fig. 4b is a SAED pattern taken from the sample annealed at 1050 °C. In addition to the diffraction spots from the silicon substrate, another set of diffraction spots appears, which is from the crystallized gadolinium silicate layer. More SAED work need to be done to determine the crystal structure of the gadolinium silicate layer.

The as-deposited lanthanum silicate films show a similar structure as the as-deposited gadolinium silicate film: e.g. a 23 nm thick amorphous silicate layer without an interfacial layer. After annealing at 900 °C for 2 min, a 5.5 nm thick interfacial layer is formed (Fig. 5a). However, an EELS study of this film revealed that the interfacial layer shown in Fig. 5a is not a pure SiO_2 layer, but a SiO_2-rich lanthanum silicate layer. The approximate composition of this interfacial layer is $(SiO_2)_{0.85}(La_2O_3)_{0.15}$.

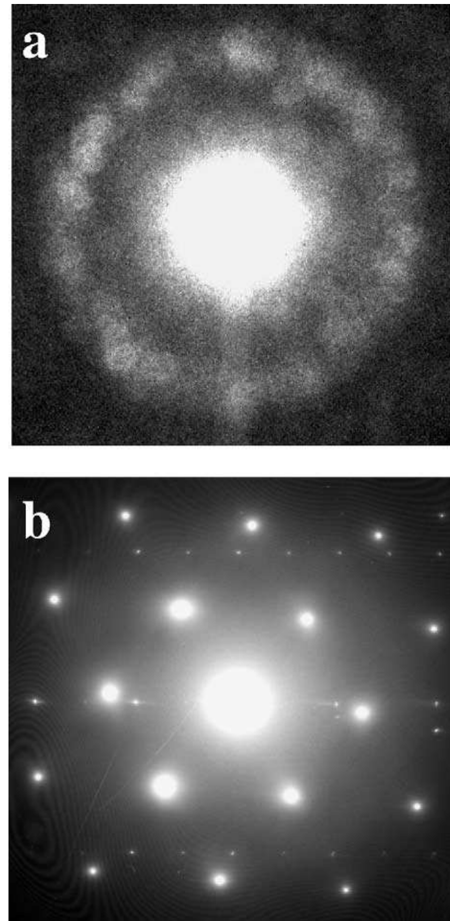


Fig. 4. SAED of the gadolinium silicate film: (a) annealed at 1000 °C in oxygen for 2 min; and (b) annealed at 1050 °C in oxygen for 15 s.

This finding suggests that diffusion of La into the SiO_2 layer already occurs at 900 °C during thermal annealing. This temperature is lower than that necessary to cause diffusion of Gd into the SiO_2. Indeed, a recent study on the structure and stability of La_2O_3/SiO_2 layers on Si(1 0 0) has shown that rapid thermal annealing at 800 °C resulted in La diffusion into the SiO_2 [9]. It is also noted that the HRTEM image contrast of the interfacial layers for gadolinium and lanthanum silicate films is different (cf. Figs. 1b and 5a), which is a result of the different chemical composition for these two layers: pure SiO_2 for Fig. 1b and $(SiO_2)_{0.85}(La_2O_3)_{0.15}$ for Fig. 5a. HRTEM and SAED studies on samples annealed at various temperatures of 850, 900, 950, 1000 and

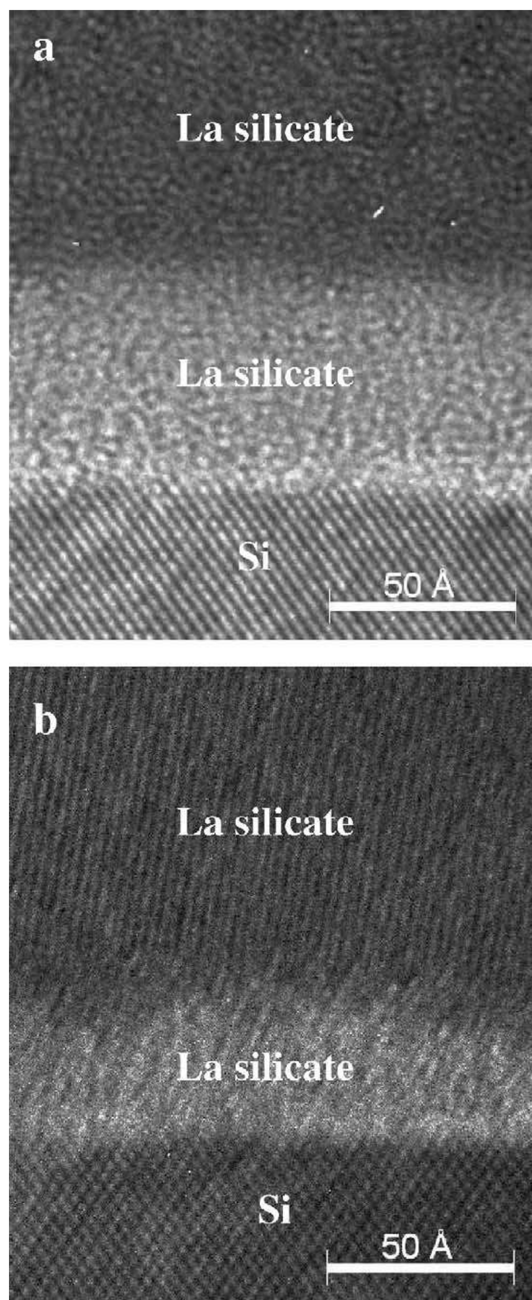


Fig. 5. HRTEM images of a 23 nm thick lanthanum silicate film: (a) annealed at 900 °C in oxygen for 2 min; and (b) annealed at 950 °C in oxygen for 30 s.

1050 °C show that the crystallization temperature for lanthanum silicate films is between 900 and 950 °C, which is lower than that of gadolinium silicate films. Fig. 5b shows the HRTEM image of the sample annealed at 950 °C: a crystallized lanthanum layer and an amorphous lanthanum silicate interfacial layer are visible. The crystallization temperature for $La_{0.23}Si_{0.14}O_{0.63}$ (i.e. 55% SiO_2 + 45% La_2O_3) in this study is in agreement with the results reported by Kingon et al. [10].

It has been shown that both gadolinium and lanthanum silicates react with silicon dioxide during high-temperature annealing, but the reaction of lanthanum silicate with SiO_2 is easier than that of gadolinium silicate. This finding is in agreement with some recent studies. Liang et al. [11] 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 silicates from SiO_2 and the metal oxide. 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 SiO_2 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 post-deposition oxygen annealing. This trend has also been observed during the formation and annealing of rare-earth oxide films [12]. The more negative enthalpy change for the formation of the lanthanum silicate also correlates with the lower crystallization temperature (900–950 °C) for the lanthanum silicate film when compared with the gadolinium silicate film (1000–1050 °C).

It is interesting to note that the thickness of the interfacial layer is 5.5 nm for the 23 nm thick lanthanum silicate film, while it is 3.4 nm for the 30 nm thick gadolinium silicate film, i.e. the thickness of this interfacial layer decreases with an increase in the original silicate layer thickness. Since the silicon substrate reacts with oxygen mainly diffused from the annealing atmosphere through the silicate layer to form the SiO_2 interfacial layer, the thicker the original silicate layer, the more difficult it is for the oxygen to diffuse, which results in a decreased thickness of this interfacial layer. Another possible reason

responsible for this phenomenon is that the ionic radius of rare-earth elements decreases with increasing atomic number, the lanthanum silicate may have larger interatomic spaces than gadolinium silicate [12], which could make the oxygen diffusion in the former easier.

4. Conclusions

1. Both gadolinium and lanthanum silicate films have a similar structure as-deposited by electron-beam evaporation: an amorphous silicate layer without an interfacial layer.
2. After annealing in oxygen at 900 °C for 2 min, an amorphous interfacial layer is formed for both gadolinium and lanthanum silicate films. This interfacial layer is pure SiO_2 for the gadolinium film, while it is a SiO_2-rich lanthanum silicate film for the lanthanum film. The formation of interfacial silicate layers is found to be easier for the lanthanum films than for the gadolinium films.
3. The crystallization temperature for the gadolinium silicate films is between 1000 and 1050 °C, while the lanthanum silicate films crystallize at a temperature between 900 and 950 °C.

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