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Thermal stability of Er_2O_3 thin films grown epitaxially on Si substrates

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The thermal stability of Er_2O_3 thin films grown epitaxially on Si substrates has been investigated in this paper by x-ray diffraction and high resolution transmission electron microscopy. The $Er_2O_3/Si(001)$ films are found to react with Si to form silicates at the temperature of 450 °C in N_2 ambience, whereas O_2 ambience can prevent the silicate formation even at the temperature of 600 °C. However, at a high temperature of 900 °C in either N_2 or O_2 ambience, Er_2O_3 films react with Si, and both silicate and SiO_2 are formed in the films. In addition, the Er_2O_3 films grown on Si(111) substrates show poorer thermal stability than those grown on Si(001) substrates; Er silicide is formed at the interface in the films annealed at 450 °C in O_2 ambience, which is attributed to that the reaction product hexagonal $ErSi_2$ is formed more easily on Si(111) than on Si(001) due to structure similarity as well as small lattice mismatch. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2712144]

I. INTRODUCTION

High-*k* dielectrics are being considered as possible replacements for SiO_2 of the gate oxide of the complementary metal-oxide-semiconductor (CMOS) devices. Apart from the common electrical requirements such as a high dielectric constant, a low gate current, and a low interface state density, good thermal stability is also very important for an ideal high-*k* material. It is not only the demand of the device work environment but also the demand of the CMOS manufactural process. A particularly demanding step in the conventional CMOS process flow is the 900–1000 °C dopant drive-in annealing. The stability of high-*k* oxides under postdeposition annealing is crucial to guarantee compatibility with the integration step.[1] In thermal process, various atmospheres will be used, such as forming gas ($N_2:H_2$), N_2, Ar, O_2, N_2O, and vacuum. Extensive studies about the annealing effect of high-*k* materials such as Al_2O_3,[2] ZrO_2,[3] and HfO_2 (Refs. 4 and 5) have been reported; an excellent review about this aspect has been given by de Almeida and Baumvol.[6]

Because the theoretical studies show that they have high dielectric constant and good thermal stability, rare earth (RE) oxides such as Pr_2O_3 (Refs. 7 and 8) and Y_2O_3 (Refs. 9 and 10) have attracted more and more attention as the candidates of high-*k* materials. Some papers dealing with interfacial layer formation and thermal stability of RE oxide films on Si substrates such as Nd_2O_3 (Ref. 11), Gd_2O_3 (Ref. 12) have been published. Recently, Er_2O_3 thin films were grown by several groups with different techniques.[13–15] Among them, the Er_2O_3 films grown epitaxially on Si substrate with an equivalent oxide thickness of 2 nm have been realized, which reveals a good electrical property.[16] To check whether epitaxially grown Er_2O_3 is an ideal high-*k* material, the knowledge on its thermal stability is needed. Ten years ago, Hubbard and Schlom[17] gave a theoretical analysis on the thermal stability of the majority of binary oxides. In their paper, the thermal stability of Er_2O_3 film was not included because the thermodynamic data of Er_2O_3 were not available. Up to now, the thermal stability of Er_2O_3 thin films grown epitaxially on Si substrates has not been reported. In this study, by a series of annealing experiments under various conditions, the thermal stability of Er_2O_3 films grown epitaxially on Si substrates was illuminated, and the reactions of the Er_2O_3 film with Si substrate under different conditions were investigated.

II. EXPERIMENT

Approximately 8 nm thick Er_2O_3 thin films were grown on 1.5 in., *p*-type Si(001) and Si(111) wafers by molecular beam epitaxy (MBE) with the substrate temperature of 700 °C. Molecular oxygen was introduced into the growth chamber through a flowmeter and a leakage valve. The details on growth have been reported in our previous publication.[15] After deposition, the samples were annealed at various temperatures and under different ambiences. The structures of the thin films and the interfaces between the films and Si substrates were investigated by x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM).

III. RESULTS AND DISCUSSION

Firstly, the cross-sectional HRTEM images of the film show a very sharp interface layer between the Er_2O_3 layer and Si substrate.[16] These results indicate that as-grown Er_2O_3 films on Si(001) have a single crystal structure and a good interface with Si, which allows us to easily clarify the interface reactions that occur in thermal processes. Figures 1(a) and 1(b) show the XRD patterns of the Er_2O_3 thin films annealed at 450 °C for 30 min in O_2 and N_2 ambiences, respectively. In Fig. 1(a), there is only one diffraction peak observed at 48.8°, which corresponds to the cubic phase $Er_2O_3(440)$ diffraction, whereas a silicate peak can be clearly observed in Fig. 1(b). This indicates that in N_2 ambience even at the temperature as low as 450 °C, Er_2O_3 films are

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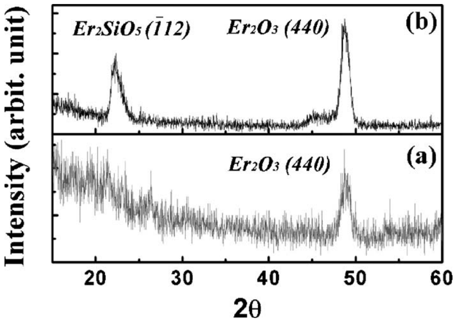

FIG. 1. XRD patterns of the Er_2O_3 thin films annealed at 450 °C for 30 min in different ambiences. (a) In O_2 ambience and (b) in N_2 ambience.

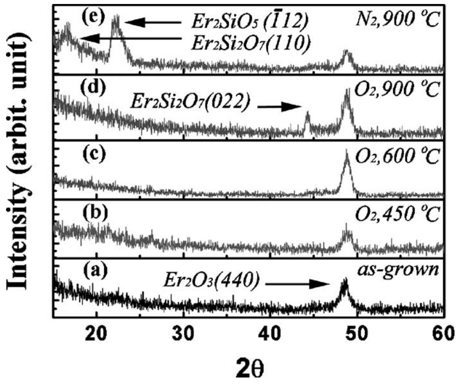

FIG. 3. XRD patterns of the Er_2O_3 thin films as-grown, annealed in O_2 ambience for 30 min at different temperatures, and annealed at 900 °C in N_2 ambience for 25 s.

not stable and react with Si at the interface to form silicates. However, if the film is annealed in O_2 ambience instead of N_2, no silicate will be formed. It seems that the films are more stable in O_2 ambience. To confirm this conclusion, the cross-sectional HRTEM observation is carried out on the sample annealed at 450 °C in O_2 ambience in order to exclude any other amorphous phase such as SiO_2 in the films or at the interface, which is very hard to be observed by XRD. Figures 2(a) and 2(b) show the cross-sectional HRTEM images of the sample before and after annealing in O_2 ambience at the temperature of 450 °C for 30 min, respectively. No difference could be found in these two cases. So it can be concluded that the oxygen ambience can prevent the film from reacting with Si substrate and the Er_2O_3 films show more stability in O_2 ambience.

To further investigate the thermal stability of the Er_2O_3 films in O_2 ambience, the films are annealed in O_2 ambience for 30 min at higher temperatures of 600 and 900 °C. As shown in Figs. 3(a)–3(d), for the samples annealed at 450 and 600 °C, no other noticeable x-ray diffraction peak is observed except for the Er_2O_3(440) peak, indicating that neither silicate nor silicide is formed in the Er_2O_3 film after annealing at 600 °C. For the sample annealed at 900 °C, a peak at 44.26° in XRD pattern is clearly observed, which probably can be attributed to Er silicate $Er_2Si_2O_7$(022) diffraction, indicating that silicate is formed at this temperature and the films are not stable in O_2 ambience at the temperature of 900 °C.

Next, rapid thermal annealing (RTA) at 900 °C for 25 s in N_2 ambience has been carried out on the film in order to investigate whether the thin film is compatible with the industrial process, as RTA process is often used in the metal-oxide-semiconductor field-effect transistor (MOSFET) manufactural process. Figure 3(e) shows the XRD patterns of the Er_2O_3 thin film before and after RTA. Before RTA, as shown in Fig. 3(a), only Er_2O_3(440) diffraction peak is observed. After RTA, besides Er_2O_3 peak, two additional peaks are clearly observed, as shown in Fig. 3(e), which are attributed to the Er silicates of Er_2SiO_5 and $Er_2Si_2O_7$, indicating the formation of silicates in the RTA process. The silicate peaks have stronger intensity than the oxide peak, which probably indicates the extensive conversion from oxide to silicates in the film. Figure 4 shows the cross-sectional HRTEM images of the Er_2O_3 thin films after RTA. An amorphous interface layer is clearly observed, indicating that an amorphous silicon oxide or an amorphous Er silicate layer is formed after RTA at 900 °C in N_2 ambience for 25 s. For the sample annealed at 900 °C in O_2 ambience for 30 min, similar results are observed with Er silicate or SiO_x formed in the films. So Er_2O_3 films grown epitaxially on Si(001) substrates are unstable at the temperature of 900 °C in either N_2 or O_2 ambience. From that point, it is not compatible with the current CMOS manufactural process.

For comparison, the thermal stability of the Er_2O_3 thin films grown epitaxially on Si(111) substrates was also investigated. For the as-grown sample, a very good single crystal structure and a very sharp interface were confirmed by cross-

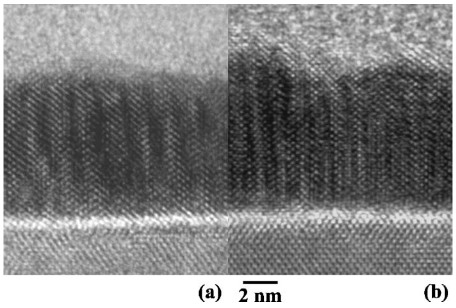

FIG. 2. Cross-sectional HRTEM images of the Er_2O_3 thin films on Si(001) substrates. (a) The as-grown films and (b) the films after annealing at 450 °C in O_2 ambience for 30 min.

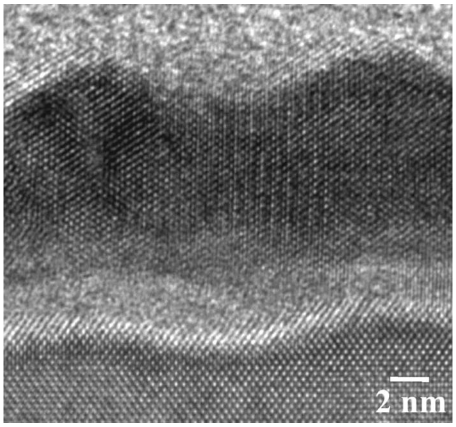

FIG. 4. Cross-sectional HRTEM image of the Er_2O_3 thin films on Si(001) after RTA at 900 °C in N_2 ambience for 25 s.

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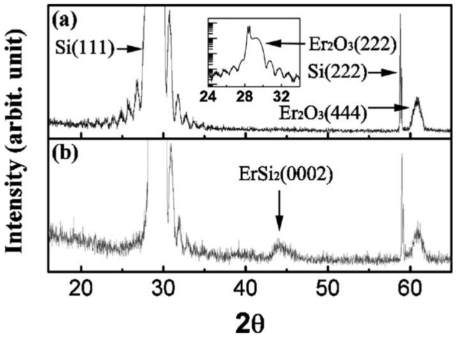

FIG. 5. XRD patterns of the Er_2O_3 thin films grown on Si(111) substrates. (a) The as-grown films and (b) the films after annealing at 450 °C in O_2 ambience for 30 min.

sectional HRTEM images (not shown here). Figure 5 shows the XRD patterns of the Er_2O_3 films before and after annealing at the temperature of 450 °C in O_2 ambience. Before annealing, except the Si(111) peak at 28.4° and Si(222) peak at 58.9°, in a wide angle range, only $Er_2O_3(444)$ and $Er_2O_3(222)$ peaks appear at 60.8° and 29.3°, respectively. The latter is much broader than Si(111) and located at the higher angle side of Si(111), as shown in the inset of Fig. 5(a). It is noteworthy that at both sides of Si(111) peak, many oscillation peaks are clearly observed, which are attributed to interference fringes of Er_2O_3 films, reflecting a smooth interface and a smooth surface of the Er_2O_3 film. After annealing, as shown in Fig. 5(b), a peak at 44.3° in XRD patterns is attributed to Er silicide $ErSi_2$ (0002) diffraction. According to the previous research, Er silicide can be easily epitaxially grown on Si.[18–20] The silicide epitaxial orientation on Si (111) is $ErSi_2(0001)$, and the corresponding XRD peak is at the position of 44.26°. Due to the epitaxial growth, other peaks corresponding to silicide are not observed. It is in contrast to the Er_2O_3 films grown on Si(001) substrate, in which no significant interface reactions are observed during annealing at the same condition. It is believed that silicide $ErSi_2$ is formed more easily at the interface on Si(111) substrate than on Si(001) due to structure similarity as well as small lattice mismatch. The basic $ErSi_2$ structure is hexagonal with the lattice parameters: $a_{hex}=0.379$ nm and $c_{hex}=0.4085$ nm. The surface of Si(111) has a hexagonal symmetry. The lattice parameters on the $ErSi_2(0001)$ hexagonal plane nearly match those on the Si(111) planes (0.384 nm) with the orientation relations of $(111)_{Si}//(0001)_{ErSi_2}$, $[1\bar{1}0]_{Si}//[10\bar{1}0]_{ErSi_2}$, and $[0\bar{1}1]_{Si}//[1\bar{1}00]_{ErSi_2}$.[20] The lattice mismatches along both directions of $[1\bar{1}0]_{Si}$ and $[0\bar{1}1]_{Si}$ are as low as 1.3%, which favors hexagonal $ErSi_2$ epitaxial growth on Si(111). However, the surface of Si(001) has a tetragonal symmetry instead of a hexagonal symmetry. As reported,[19] the hexagonal $ErSi_2$ epitaxy on Si(001) substrate follows the orientation relations of $(001)_{Si}//(0\bar{1}10)_{ErSi_2}$, $[110]_{Si}//[0001]_{ErSi_2}$, and $[\bar{1}10]_{Si}//[2\bar{1}\bar{1}0]_{ErSi_2}$. Although the lattice mismatch along the direction of $[\bar{1}10]_{Si}$ is still as low as 1.3%, however, the lattice mismatch along the direction of $[110]_{Si}$ is as large as 6.5%.

IV. CONCLUSION

In summary, annealing experiments under various conditions have been done to investigate the thermal stability of Er_2O_3 thin films grown epitaxially on Si substrates. Due to interface reactions the films are unstable at high temperatures. The $Er_2O_3/Si(001)$ films are found to react with Si substrates to form silicates at the temperature of 450 °C in N_2 ambience, whereas O_2 ambience can prevent the silicate formation at this temperature. However, at a high temperature of 900 °C in either N_2 ambience or O_2 ambience, the Er_2O_3 films react with Si to form Er silicate and SiO_2. The Er_2O_3 films grown on Si(111) substrates have poorer thermal stability than those grown on Si(001) substrate. The reason may be attributed to that the hexagonal $ErSi_2$ is formed more easily on Si(111) than on Si(001) with structure similarity as well as small lattice mismatch.

ACKNOWLEDGMENTS

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