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P4-5

Thermal Stability of HfO_2/Ultrathin-SiO_2/Si Structures

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1. Introduction

Thermal stability of high-*k* gate dielectrics on a Si substrate is a crucial issue for integrating these materials into the standard MOSFET, because the gate dielectrics must withstand thermal annealing, e.g. dopant activation (900-1000°C). HfO_2 is a prospective candidate as well as ZrO_2. It is expected that the HfO_2 film on Si is similar in thermal property to the ZrO_2. The ZrO_2 shows two problematic phenomena: the growth of Si oxide or silicate at the high-*k*/Si interface [1-4], and the formation of silicide at high temperature (>900°C) [2,4,5]. The former results in high EOT (equivalent oxide thickness), and the latter apparently loses the dielectric nature. Consequently, we should carefully choose the annealing conditions, but the process window for the HfO_2 film was not determined in detail. In this work, we examine the structural change of HfO_2/ultrathin-SiO_2/Si system due to the thermal annealing under various O_2 pressures.

2. Experimental

Sample preparation was carried out by using an ultrahigh-vacuum (UHV) electron-beam deposition system. Firstly an n-type Si(100) sample was heated at 900°C under the UHV conditions to expose the clean Si surface. An ultrathin SiO_2 layer, about 0.3 nm, was then thermally grown at 650°C in 2×10^{-6} Torr O_2 for 10 minutes. The 2.6-nm-thick HfO_2 film was deposited on the SiO_2 at 400°C by using an evaporation of metallic Hf in 2×10^{-6} Torr O_2. For the thermal annealing and surface analysis, we used an UHV surface-analysis system connected with an UHV preparation chamber. The samples were annealed at 500-1000°C in 1×10^{-4}-10^{-7} Torr O_2 for 3 minutes, and then examined by using XPS (x-ray photoelectron spectroscopy), SEM (secondary electron microscopy), and μ-AES (microprobe Auger electron spectroscopy).

3. Results and Discussion

Figure 1 shows the typical Si 2p and Hf 4f XPS spectra observed from the annealed samples. The spectra shown in Fig 1(a) are quite the same as those for the as-grown sample (not shown), representing that the HfO_2/SiO_2/Si structure is stable under this annealing condition. By increasing the O_2 pressure, the oxide component of the Si 2p spectrum shown in Fig. 1(b) apparently increases, which was assigned to Si 4+ (SiO_2). In this case, the SiO_2 layer was estimated to be about 2 nm. This result was consistent with the XTEM image, showing that the 2-nm-thick SiO_2 grew at the HfO_2/Si interface. The O_2-pressure and temperature dependences of the interfacial SiO_2 shown in Fig. 2(a) indicate that the oxidation is sensitive to the O_2 pressure. It is obvious that the high vacuum conditions are required to suppress the interfacial oxidation. On the other hand, the Si 2p and Hf 4f spectra shown in Fig. 1(c) indicate that the interfacial Si oxide decomposes and the Hf silicide is formed at 900°C in 1×10^{-6} Torr O_2. Figure 2(b) indicates that the silicidation takes place at temperatures above 900°C. The gray region in Figs. 2(a) and 2(b) corresponds to the process window determined by XPS, in which the HfO_2/SiO_2/Si structure is stable. This result suggests that the thermal treatment of HfO_2 film requires the high vacuum (~10^{-7} Torr) and lower temperature (<900°C) conditions. On the contrary, a standard MOSFET with HfO_2 gate dielectrics was recently demonstrated, which was fabricated by the conventional process including a dopnat activation at 900-1000°C [6]. This is obviously inconsistent with the process window as determined by XPS.

Figure 3 shows the SEM image and μ-AES spectra observed from the HfO_2 surface annealed at 900°C in 1×10^{-6} Torr O_2. The dark circles with several tens μm in diameters are observed, which show clear Si and weak Hf

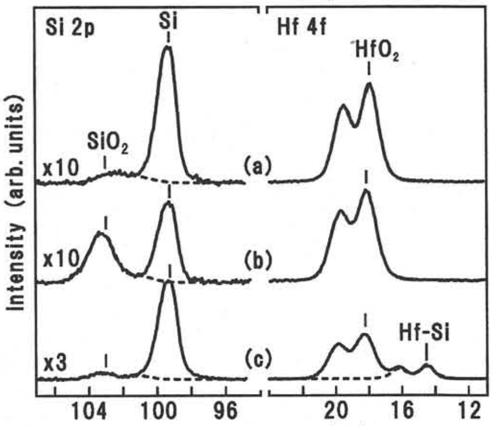

FIG.1 Si 2p and Hf 4f XPS spectra for the various annealing conditions. (a) 800°C, $1\text{x}10^{-7}$ Torr. (b) 800°C, $1\text{x}10^{-5}$ Torr. (c) 900°C, $1\text{x}10^{-6}$ Torr.

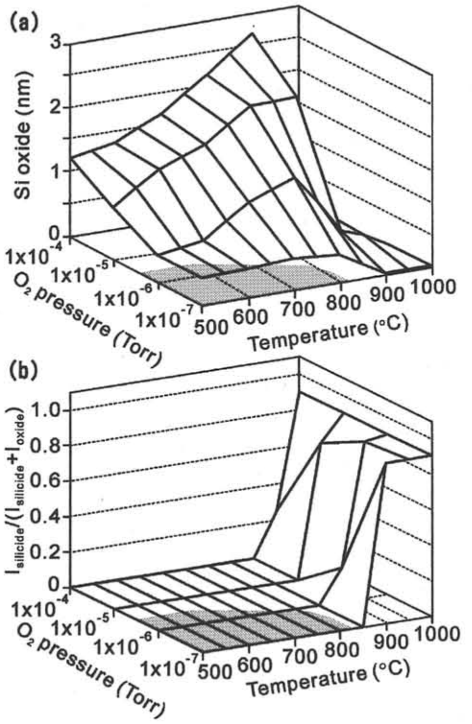

FIG.2 O_2 pressure and temperature dependences of (a) interfacial Si oxidaiton, and (b) silicidation.

AES peaks representing the formation of Hf silicide. The surrounding bright area shows clear Hf and O AES peaks, but does not show the Si peak. Thus, the HfO_2 layer remains around the silicide circles. We also observed that the silicidation proceeds as a two-dimensional (2D) expansion of the silicide circles, as schematically shown by Fig. 4(a). Here, we consider the thermal stability for the case of actual MOSFET. Because the poly-Si layer that covers the HfO_2 surface suppresses the O_2 incorporation into the HfO_2/Si inteface [4], the interfacial oxidation is expected to be suppressed. However, this poly-Si layer can not prevent the silicidaiton [4]. On the other hand, actual gate area of the HfO_2 film is less than μm^2. In this case, the silicidation is also expected to be avoidable as shown by the process in Fig. 4(b). If a part of the patterned HfO_2 areas has silicide nuclei, the silicidation proceeds like a case of non-pattered film, while the other parts of the patterned areas which have no nuclei remain thermally stable without silicidation, if the edge of HfO_2 area is terminated by appropriate stable materials. As a result, some patterned areas survive under higher temperature annealing. In this idea, the nucleus density is an important factor which determines the probability of failure due to the silicidation. From the SEM observation, the nucleus density was estimated to be less than 1×10^3 cm^{-2}. Therefore, most of sub-μm^2 HfO_2 patterns can survive. However, from a viewpoint of ULSI fabrication, it is obvious that the silicidation is a crucial problem. We consider that the control of silicide nucleation is essential to apply the HfO_2 to ULSI devices.

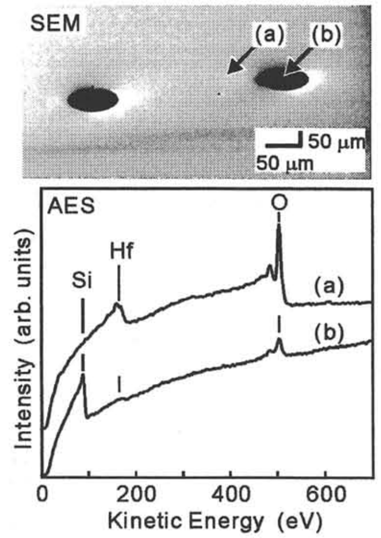

FIG.3 Formation of Hf silicide (dark area) observed by SEM and μ-AES.

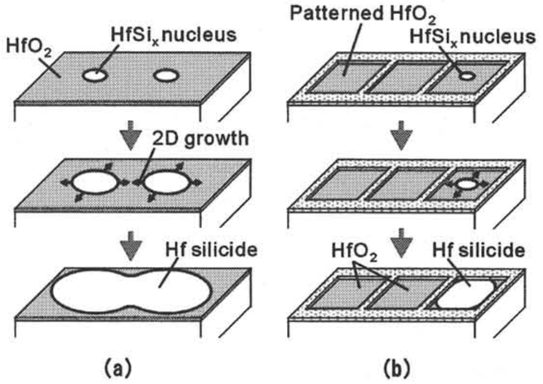

FIG.4 Silicidation for a non-patterd-HfO_2 layer (a) and a pattered-HfO_2 (b).

4. Conclusion

Thermal treatment of HfO_2/Si structure requires high vacuum conditions (~10^{-7} Torr) to suppress the interfacial Si oxidation. Also, the silicidation proceeds in a 2D manner at temperatures higher than 900°C. We suggested that the control of the silicide nucleation is important for realizing HfO_2 gate stack structures.

Acknowledgments

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