Annealing Behavior of La$_2$O$_3$ Thin Film Deposited on Si (001) Substrate Studied by Spherical Aberration Corrected TEM/STEM

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The annealing behavior of an La$_2$O$_3$ thin film deposited on an Si (001) substrate was studied by spherical aberration corrected transmission electron microscopy. The thickness and roughness of the as-deposited and 300/500°C post-deposition annealing (PDA) films was measured precisely. Composition analysis of the films was performed by electron energy loss spectroscopy. Based on the results, we propose a model for atomic diffusions and reactions during the PDA. We clarify the reason that the 300°C PDA brings better electric properties than the as-deposition and the 500°C PDA.

Key words: lanthanum oxide, high-k, transmission electron microscopy, spherical aberration correction

1. INTRODUCTION

The scale-down of metal-oxide-semiconductor field effect transistors (MOSFETs) requires a reduction in the thickness of gate dielectrics such as SiO$_2$. Presently, they have reached atomic scale, which causes large leakage currents due to direct tunneling [1]. This problem can be solved by replacing the SiO$_2$ or Si-oxynitride with other materials with higher dielectric constants, so-called, high-k materials [2, 3]. Of the various high-k materials, La$_2$O$_3$ is considered a promising candidate for future gate dielectrics because of high dielectric constant, large conduction band offset, and high mobility in the channels [4, 5]. In the present study, we studied La$_2$O$_3$ thin films deposited on Si (001) substrates by using a spherical aberration (Cs) -corrected electron microscope (EM) [6]. The annealing behavior of the films is discussed based on the experimental results.

2. EXPERIMENTAL

After removing a surface oxide layer on an Si (001) substrate by diluted HF solution, La$_2$O$_3$ is deposited by electron-beam evaporation at room temperature. Then, post-deposition annealing (PDA) is performed for 5 min at 300 or 500°C in nitrogen ambient (1 Torr). The as-deposited and 300°C and 500°C PDA samples are thinned for cross-sectional EM observations by mechanical polishing and the 3 kV Ar-ion milling. The samples are examined by transmission electron microscopy (TEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and electron energy loss spectroscopy (EELS). A transmission electron microscope (JEM-2100F) equipped with two Cs-correctors for the illumination system and the imaging system is used in the present study.

3. RESULTS

It is known that in a conventional TEM without Cs-correction, Fresnel fringes and overlapping of lattice fringes appear around interfaces and make it rather difficult to detect positions of the interfaces with lattice-resolution. In contrast, by using Cs-corrected TEM, the above artifacts can be removed [7]. Therefore, positions of interfaces can be detected precisely. Figure 1 shows a Cs-corrected TEM image of the 300°C PDA sample. The dielectric films consist of a bright and another dark amorphous layers, which are called Si-rich and La-rich layers, respectively in the present study. The layers are formed in all the samples.

Figure 2 (a) shows an area in the 300°C PDA sample which is thinned within several nm. Figure 2 (b) exhibits an intensity profile across the gate stack in Fig. 2 (a), in which the positions of the interface and the La-rich/Si-rich interface can be detected precisely. Based on such profiles acquired at several different positions, the thickness of the La-rich layer (T$_{La}$) is measured for each sample. T$_{La}$ of the as-deposited sample is 4.1 nm. Though T$_{La}$ does not change after the 300°C PDA, it decreases by about 0.3 nm after the 500°C PDA. Also root mean square (RMS) of the roughness at the surface (R$_1$) and the La-rich/Si-rich interface (R$_2$) are measured from the profiles. R$_1$ and R$_2$ in the as-deposited sample are 0.4 and 0.3 nm, respectively. These values in the 300°C PDA sample are almost equivalent to those of the as-deposited sample, while they increase drastically after the 500°C PDA.
Figure 1 Cₐ-corrected TEM image of a La₂O₃/Si interface after the 300°C PDA.

Figure 2 (a) Cₐ-corrected TEM image of the 300°C PDA sample. The area in the field of view is thinned within several nm. (b) Intensity profile across the gate stack, in which the positions of surfaces and La-rich/Si-rich interfaces can be detected precisely.

Figure 3 (a) shows a Cₐ-corrected HAADF-STEM image of the 300°C PDA sample. Advantages of Cₐ-correction in STEM are not only an improvement in spatial resolution but also a reduction of the acquisition time, which means effectively a reduction of the specimen drift during the image acquisition [8]. In the present study, Cₐ-corrected STEM is used in order to suppress influences of the specimen drift to STEM images, which is very important for precise measurements of the thickness of each layer. Figure 3 (b) shows an intensity profile across the gate stack in Fig. 3 (a). In the profile, the intensity changes continuously between dotted lines shown in Fig. 3 (b). Because STEM images reflect projections of sample structures to incident directions of electron beams, it is considered that the intensity slope comes from the superposition of contrasts from the Si-rich layer and the Si substrate owing to the interfacial roughness. Therefore, this width reflects the roughness at the Si-rich/Si interface (R₃). As the results of the estimation as mentioned above, R₃ of the as-deposited sample is 0.4 nm, while those of the 300°C and 500°C PDA samples are 0.6 nm.

Figure 3 (a) Cₐ-corrected HAADF-STEM image of a La₂O₃/Si interface after 300°C PDA. (b) The intensity profile across the gate stack.

In TEM images, fringe contrast of a crystalline lattice is generally much stronger than that of an amorphous structure. Therefore, the edge of the lattice fringe shown by “P” in Fig. 4 corresponds to not the average position of the rough amorphous/crystalline interface but the front edge of the Si substrate. The thickness of the Si-rich layer (Tₛ) is estimated by sum of the width W (in Cₐ-corrected TEM images) and half of the width R₃ (in Cₐ-corrected HAADF-STEM images). Based on the above consideration, Tₛ of the as-deposited, 300°C PDA, and 500°C PDA samples are measured to be 0.9, 1.2, and 1.5 nm, respectively.
Figure 5 shows elemental profiles across the gate stack measured by STEM-EELS. These profiles are produced by the integration of the spectra signals in the energy ranges of 98.0-102.9 eV for Si, 528.6-555.2 eV for O, and 832.2-858.8 eV for La. The above range for Si is set to include only vicinity of the onset energy for L-edge of crystalline silicon, in order to suppress the influence of La N-edge appearing around 108 eV. Since Si L-edges in various compounds as well as La N-edge appear at the higher energies than the range, the Si profiles in Fig. 5 reflect amount of pure silicon only. In Fig. 5, kinds of plateaus in the O profiles appear in the La-rich layers, the heights of which reflect the composition ratios of O in the layers. Comparing the heights in Fig. 5 (a)-(c), it turns out that the O ratio increases by about 1.6 times after the 300°C/500°C PDA. The peaks in the La profiles are located at the same positions as the plateaus in the O profiles. The peak heights reflect the composition ratios of La in the La-rich layers, which increases by about 1.2 times after the 500°C PDA, though it hardly changes after the 300°C PDA. Owing to the more increase of O than La in the La-rich layer, La/O ratio after the 500°C PDA is lower than before the PDA.

The chemical shifts of La M-edges are also analyzed in order to decide whether the La-rich layers are silicate or oxide. In the all samples, the edges appear at the same energy loss position, which is about 3 eV higher than that in La2O3 [9]. It means that the La-rich layers become silicate as the result of a diffusion of silicon atoms from the Si substrate.

4. DISCUSSIONS

Based on all the experimental results, we propose a model for atomic diffusions and reactions in the present samples as follows. When La2O3 is deposited on the Si substrate at room temperature, Si, La, and O atoms react each other on the surface. As the result, the La-rich and

Figure 4 Precise detection of thickness and both edges of the Si-rich layer in a C-corrected TEM image.
the Si-rich layers are formed. Because the composition ratio of O in the La-rich layer is much lower than that in La₂O₃, a number of oxygen defects are contained in the film, which causes the trap sites. It is considered that they are responsible for the high leakage current and the low mobility in the as-deposited sample due to Coulomb scattering [10, 11].

During the PDA processes, the oxygen defects in the films are reduced due to an absorption of the residual oxygen in the N₂ ambient. As the results, the mobility increases and the leakage current decreases. During the 500 °C PDA process, La and Si atoms diffuse extensively into the La-rich layer, which induces roughening of the surface and the La-rich/Si-rich interface. The decrease of Ti and the increase of La and O composition ratios in the La-rich layer after the 500°C PDA mean that Si atoms are excluded from the La-rich layer. It indicates that a part of La-O-Si bonds are replaced with La-O-La bonds. It is known that highly polarizable bonds, for example La-O-La bonds, in the dielectric films lead to remote phonon scattering of carriers [12]. Finally the channel mobility is low due to Coulomb scattering before the PDA, and due to remote phonon scattering and remote roughness scattering after the 500°C PDA. Thus, the mobility in the 300°C PDA sample is higher than those in the as-deposited and the 500°C PDA samples.

5. CONCLUSIONS

The annealing behavior of the La₂O₃ thin films on the Si (001) substrate was studied by using a Cs-corrected EM. The films were split in two amorphous layers called La-rich and Si-rich layers. The roughness at the surface/interfaces and the thickness of the layers were measured precisely by the combination of TEM and HAADF-STEM images. Based on the result of the measurements and the elemental analyses by EELS, a model for atomic diffusions and reactions was proposed. We clarified the reason that the higher mobility was achieved by the 300°C PDA than as-deposition and the 500°C PDA.

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