Extended Abstracts of the 2001 International Conference on Solid State Devices and Materials, Tokyo, 2001, pp. 500–501

B-9-3

Scanning Tunneling Microscopy Study of Hf Silicate Formed by Ulttrathin Hf Metal on SiO_2:Effect of Hf/SiO_2 Thickness Ratio

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1. Introduction

Recently, many high-k materials [1-9] like $Hf(Zr)O_2$, $Hf(Zr)Si_xO_y$, Al_2O_3, La_2O_3, Y_2O_3, Gd_2O_3, $GdSi_xO_y$, and Pr_2O_3 have been introduced as an alternative gate dielectrics to overcome the leakage current issue of SiO_2. In a view of thermal stability, however, high-k oxides would be avoided due to their practical metastability [1,5] showing silicate formation far below the thermal budget required to decompose based upon thermodynamic data. Particularly, in light of the fact that as closer to oxide/Si interface chemical bonding at the interface should be similar to SiO_2-Si interface so as to guarantee the interface reliability for successful device applications, silicate would be more probable for alternative dielectrics.

Hf forms the most stable oxide [6] with the highest heat of formation (ΔHf=271Kcal/mol) among the elements of transition IV-A group (Ti, Zr, Hf), and HfO_2 also shows a high dielectric constant of 30~40 along with a bandgap of ~5.6eV. These properties make Hf silicate one of the most promising candidates for alternative gate dielectrics.

In this paper, we present Hf silicate formation behaviors based upon ultrathin Hf metal on SiO_2 with annealing in ultrahigh vacuum (UHV) ambient by employing scanning tunneling microscopy (STM).

2. Experimental

Clean Si(001) surfaces were thermally oxidized to form 1 monolayer (ML) [10] and 1nm thick SiO_2 [11] by oxygen exposure for 3min at room temperature under 2×10^{-4}Pa O_2 pressure and by one for 60min at 740°C under 2×10^{-2}Pa, respectively. Electron-beam evaporated Hf was deposited on SiO_2 to make two splits of Hf/SiO_2 stack such as 1.7ML/1ML (Hf-rich) and 1ML/1nm (SiO_2-rich). Dielectric surfaces were observed using STM by applying a sample bias of ~5V to inject tunneling electrons into the oxide conduction band. Local surface dielectric characteristics along with bandgap were measured with scanning tunneling spectroscopy (STS).

3. Hf-rich silicate made by Hf/SiO_2 (1.7ML/1ML)

Figs. 1 (a), (b), (c), and (d) show the as-Hf deposited, 400°C, 500°C, and 780°C annealed STM topographies, respectively. Ultrathin metal deposition on oxide film has already been found to form cluster-like morphology like Fig. 1 (a) on Au/TiO_2 and Pd/MgO [12]. Average diameter of cluster tends to increase with deposited metal coverage, and the density of state near the Fermi level also increases with cluster size implying development of metallic nature. In our case using 1.7ML thick Hf, average cluster diameter of ~3.6nm has been observed with 0.11nm root-mean-square (RMS) roughness. Increasing temperature up to 700°C causes the reaction between Hf and underlying SiO_2 showing disappearance of cluster feature with increasing RMS roughness.

From previous study [11] focused on SiO_2, it has been known that the tunneling spectra taken within bias range from –6 to +6V could give useful information about local surface dielectric characteristics as well as surface bandgap. An amount of surface bandgap in 1ML thick SiO_2 is observed to be ~2.5eV compared to bulk value of ~9eV, as shown in Fig. 2.

Dielectric degradation caused by annealing at 400°C for 2min in UHV could be explained by a formation of amorphous silicide based upon previous works [13,14]. Interestingly, further annealing to 500°C restores its dielectric property, and this peculiar behavior might be understood by different activation energies of amorphous silicidation and silicate reaction. Epitaxial Hf silicide phase appears at 780°C for 2min, and tend to align along Si<110> direction. Topographic line scan in Fig.1 (e) describes the formation of Si depletion zone near silicide phases implying that diffusion species for epitaxial silicide phase should be Si atoms. Si depletion zone is usually found along with right angle kinks of Si steps.

4. SiO_2-rich Hf silicate made by Hf/SiO_2 (1ML/1nm)

Figs.3 (a), (b), (c), and (d) illustrate as-Hf deposited, 580°C, 650°C annealed STM topographies in UHV, and additionally 650°C annealed one in oxygen-rich ambient, respectively. Contrary to previous report [12], increased average cluster diameter of ~4.3nm is shown in spite of reduced metal coverage, and might be attributed to increased SiO_2 thickness. Formation of amorphous silicide at 400°C observed in Hf-rich silicate is not observed in SiO_2-rich one. Lattice image shown in Fig.3 (b) reveals an appearance of crystalline phase in 580°C annealing for 2min, and is believed to form silicate phase from STS data of Fig.4 (a). The amount of silicate bandgap is larger than one of SiO_2, and the surface bandgap narrowing to 5eV from 9eV, which usually observed when 1nm thick SiO_2 has been characterized by STS, almost disappears in case of silicate. Further annealing to 650°C in UHV drastically degrades a dielectric property due to silicidation, and additional annealing in oxygen-rich ambient enables a partial recovery of dielectric property.

5. Conclusions

Hf-rich and SiO_2-rich Hf silicate were formed by controlling the thickness ratio of Hf/SiO_2 in UHV STM chamber. Reaction temperature for silicidation was found to change with different thickness ratio, and dielectric property of silicate was improved in SiO_2-rich one compared to SiO_2.

This work was supported by NEDO.

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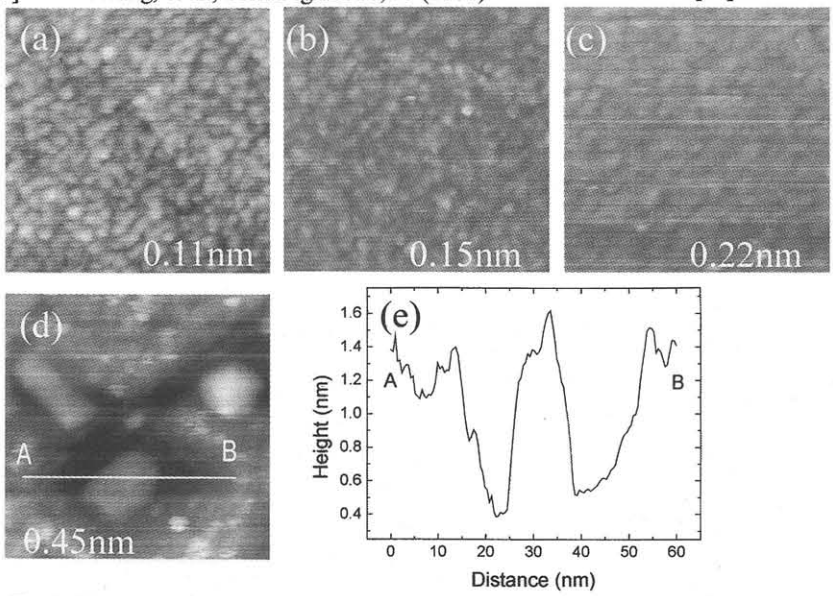

Fig.1 STM surface topographies showing (a) as-Hf deposited, (b) 400°C, (c) 500°C, and (d) 780°C annealed Hf/SiO_2 film stacks for 2min under UHV, respectively, in case of thickness ratio of 1.7ML/1ML. Topographic line scan shown in (e) is along the line AB noted in (d). RMS roughness value for each figure is indicated on the bottom corner. Scanning area is 50nm × 50nm.

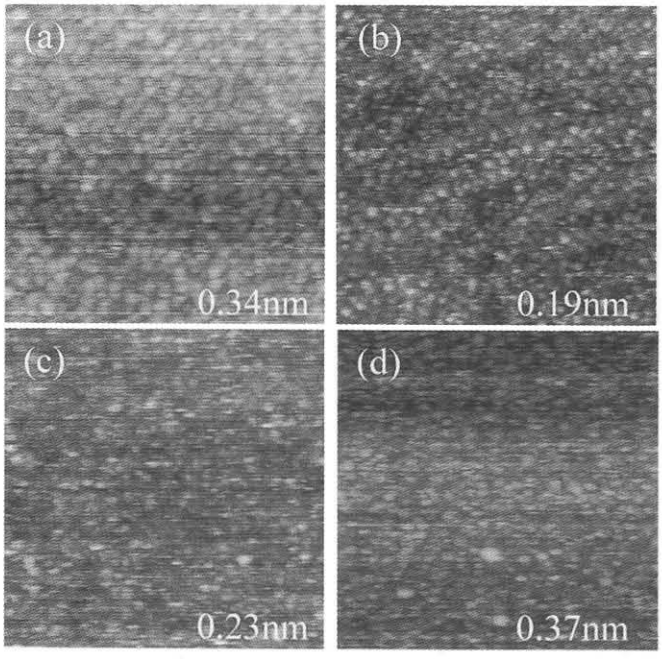

Fig.3 STM surface topographies showing (a) as-Hf deposited, (b) 580°C, (c) 650°C annealed Hf/SiO_2 film stacks for 2min under UHV, and (d) additionally 650°C annealed one for 2min under 8×10^{-2} Pa O_2 pressure, respectively, in case of thickness ratio of 1ML/1nm. Development of crystalline texture observed along with decreased roughness at 580°C is explained by the formation of SiO_2-rich silicate in assistance with Fig.4 (a). After 580°C, an amount of roughness consistently increases with thermal budget, but the additional annealing in oxygen-rich ambient partially restores crystalline texture in spite of increased thermal budget. Scanning area is 80nm × 80nm.

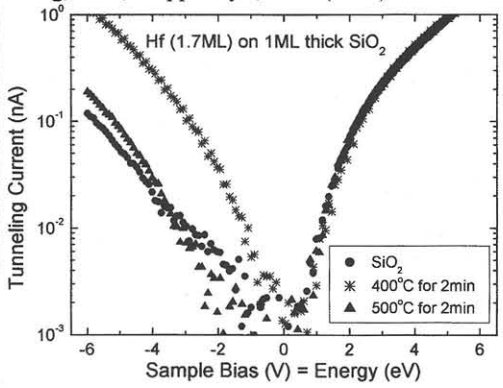

Fig.2 Log-linear I-V spectra of 1ML thick SiO_2 and annealed Hf/SiO_2 film stack measured by STS. The bias width of ~0 tunneling current region observed nearby 0V (=E_f) corresponds to the amount of surface bandgap of dielectrics. Fermi level of Hf-rich silicate formed at 500°C tends to be pinned to the conduction band edge.

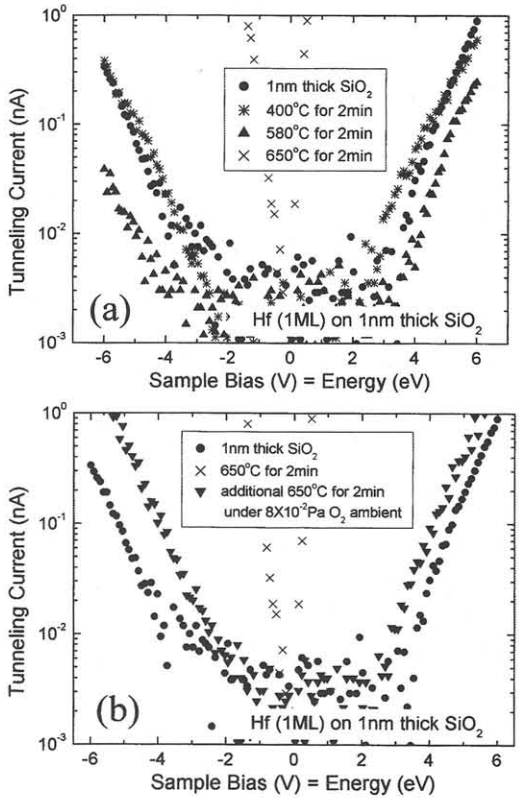

Fig.4 Log-linear I-V spectra of 1nm thick SiO_2 and annealed Hf/SiO_2 film stack measured by STS. Under SiO_2-rich condition, dielectric degradation at 400°C shown in Fig.2 disappears, and wider (~5eV) bandgap compared to 1nm thick SiO_2 is observed at 580°C annealed silicate. After additional annealing at 650°C in oxygen-rich ambient, partial recovery of dielectric property is shown in (b), and agrees well with Fig. 3 (d).