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Hf-silicidation reactions due to vacuum annealing for a-Si/ HfSiO(N)/ Si gate stack studied by synchrotron radiation photoemission spectroscopy

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Introduction

The downscaling of Si devices has reached a limitation in thickness of SiO_2 dielectric films. Therefore, high dielectric constant (high-*k*) materials are utilized as gate dielectrics instead of SiO_2. Among high-*k* materials, HfO_2, HfSiO, and HfSiON are considered as one of the most promising candidates because of their wide band gap [1]. However, there are several problems in practical use of them, such as the formation of Hf-silicide ($HfSi_2$) and the crystallization of HfO_2 during annealing for the activation processes. In order to maintain the high dielectric properties, it is necessary to elucidate the mechanism of these reactions in detail. Photoemission spectroscopy is one of the most powerful experimental techniques to analyze chemical reactions of ultra thin films. In this study, we employ it for investigating the Hf-silicidation reaction of poly-Si/HfSiO(N)/Si gate stack structures after ultra high vacuum (UHV) annealing.

Experimental

HfSiO ([N]=0 %) and HfSiON ([N]=20 %) layers were deposited on clean *p*-type Si (001) substrates by atomic layer deposition, and amorphous-Si was also deposited by magnetron sputtering. The thickness of each layer was estimated to be 2 nm by the elipsometry.

Photoemission measurements were carried out at the undulator beamline BL-2C. Sample surfaces were etched in a diluted HF solution to remove native oxides just before loading into the load lock. Each sample was annealed at 650, 700, and 800 °C for 10 min by the direct current flowing method, and then transferred to the photoemission chamber directly. Base pressure of annealing chamber was below 1×10^{-8} Torr.

Results and Discussion

Figure 1 shows the change of chemical bonding state in Hf-oxide for HfSiO and HfSiON films. At the 700 °C annealing, Hf-silicide components emerge slightly in both samples. However, quite different reactions occur at 800 °C: In the HfSiO film, Hf-silicidation proceeds completely and all the Hf-oxide components disappear. In contrast, more than half of Hf-oxide remains unchanged and Hf-nitride is formed instead of Hf-silicide in the HfSiON film. This result indicates that the rearrangement of chemical bonding occurs at Hf atoms in the HfSiON film.

Hf-silicidation between the a-Si and the dielectric film can be explained by the following reaction [1]:

$$HfO_{2-x} + (4-x)Si \rightarrow HfSi_2 + (2-x)SiO \qquad (1)$$

The effect of oxygen vacancies is taken into account in this reaction. However, the Hf-nitridation cannot be explained reasonably only by this reaction. One possible scenario is the following: Hf-silicide is formed at the upper interface at 700°C, and it reacts with nitrogen to form Hf-nitride at 800°C. As a result, Hf-nitride layer is formed between a-Si and HfSiON, which may suppress further reactions.

Although Hf-nitride is thermodynamically more stable than Hf-silicide, Hf-nitride wasn't formed at as low temperature as 700°C. This is probably because the chemical kinetics works more strongly than thermodynamics at 700°C.

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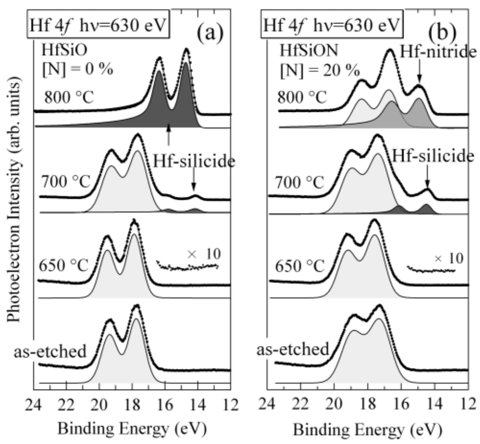

Fig. 1 Annealing-temperature dependence of Hf 4*f* core-level spectra for (a) HfSiO and (b) HfSiON.

Reference

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