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Mechanism of the interfacial reaction for polycrystalline-Si /HfO_2/Si gate stacks with UHV annealing studied by photoemission spectroscopy

Haruhiko TAKAHASHI[1*], Satoshi TOYODA[1], Jun OKABAYASHI[1], Hiroshi KUMIGASHIRA[1], Masaharu OSHIMA[1], Kazuto IKEDA[2], Guo-Lin LIU[2], Ziyuan LIU[2], and Koji USUDA[2]
[1]The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
[2]STARC, Kohoku-ku, Kanagawa 222-0033, Japan

Introduction

In previous reports, we investigated the mechanism of silicidation on annealing temperature in ultrahigh vacuum (UHV) [1]. We have found that Hf silicide ($HfSi_2$) is formed at the "upper interface" between poly-Si electrodes and HfO_2 gate dielectrics at 700 °C for 10 min. At 750 °C annealing, silicidation propagates rapidly from the upper interface to the "lower interface" between HfO_2 gate dielectrics and Si substrates. The annealing-time dependence of photoemission spectra can provide us with important information to understand the mechanism for silicidation.

Experimental

The HfO_2 layer was deposited on clean *p*-type Si (001) substrates by reactive magnetron sputtering using a Hf metal. The thickness was estimated by the elipsometry to be 2 nm for the HfO_2 layer and 0.5 nm SiO_2 interfacial layer on Si substrates. Poly-Si electrodes of 3 nm were deposited on HfO_2 gate stacks at room temperature by magnetron sputtering. Photoemission spectroscopy was carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). Annealing was performed in ultra high vacuum (UHV) by a direct-current-flowing method through the samples at 700 °C for each time just before the photoemission measurements.

Results and Discussion

We show Si 2*p* photoemission spectra for the 1 min annealing sample in Figs. 1 (a) and (b) at emission angles of 0 and 60 °, respectively. The sample is free from Hf silicide by Hf 4*f* photoemission spectra (Fig. 2). From Si 2*p* photoemission spectra, an oxide component *X* is detected. Considering its binding energy, the component *X* corresponds to a Si sub oxide. In addition, the intensity ratio of the component *X* to the component poly-Si decreases in the surface sensitive measurement, suggesting that the Si sub oxide exists below poly-Si electrodes at the upper interface.

From these results, we have found that the Si sub oxide component *X* exists at the upper interface before the silicidation. Considering that silicidation starts not at the lower interface but at the upper interface, the difference of Si oxide components at each interface can be well related to silicidation. The oxide component, nonstoichiometric Si oxide (SiO_x) exists at the upper interface whereas stoichiometric Si oxide (SiO_2) exists at the lower interface. Therefore, the SiO_x at the upper interface can trigger silicidation. Considering the reported results, silicidation occurs through the following reactions,

$$SiO_x + (x-1)Si \rightarrow xSiO\uparrow \quad (a)$$

$$HfO_2 + 4SiO\uparrow \rightarrow HfSi_2 + 2SiO_2 \quad (b)$$

(a) SiO_x at the upper interface reacts with poly-Si and SiO gas is generated. (b) SiO gas reacts with HfO_2 and silicidation may occur consequently with the SiO_2 formation [2]. Here, the SiO_x can be formed by the oxygen atom diffusion from HfO_2 to poly-Si during annealing. Consequently, oxygen vacancies are formed in HfO_2 [3].

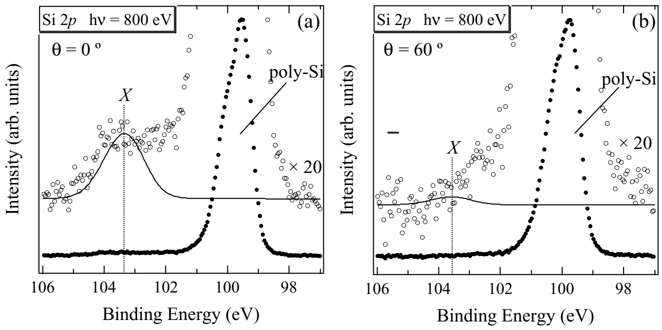

Fig. 1. Si 2*p* photoemission spectra by the 700 °C annealing for 1 min at the emission angles of (a) 0 ° and (b) 60 °.

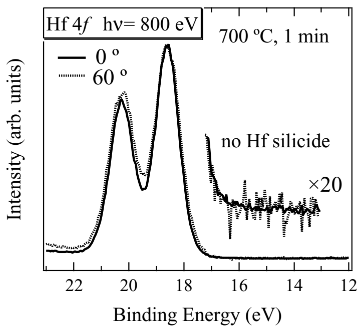

Fig. 2. Hf 4*f* photoemission spectra by the 700 °C annealing for 1 min. Solid curve shows the spectrum taken at the emission angle of 0 °. Dashed curve shows that of 60 °.

References

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*htakahashi@sr.t.u-tokyo.ac.jp