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Communication

Stability of Sputtered Hf-Silicate Films in Poly Si/Hf-Silicate Gate Stack Under the Chemical Vapor Deposition of Poly Si and by Annealing

Sung-Kwan Kang,† Robert Sinclair, and Dae-Hong Ko*

School of Material Science and Engineering, Stanford University, CA 94305, U.S.A.
**Department of Ceramic Engineering, Yonsei University, Seoul 120-749, Korea*
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ABSTRACT

We investigated the effects of SiH_4 gas on the surface of Hf-silicate films during the deposition of polycrystalline (poly) Si films and the thermal stability of sputtered Hf-silicate films in poly Si/Hf-silicate structure by using High Resolution Transmission Electron Microscopy (HR-TEM) and X-ray Photoelectron Spectroscopy (XPS). Hf-silicate films were deposited by using DC-magnetron sputtering with Hf target and Si target and poly Si films were deposited at 600°C by using Low Pressure Chemical Vapor Deposition (LPCVD) with SiH_4 gas. After poly Si film deposition at 600°C, Hf silicide layer was observed between poly Si and Hf-silicate films due to the reaction between active SiH_4 gas and Hf-silicate films. After annealing at 900°C, Hf silicide, formed during the deposition of poly Si, changed to Hf-silicate and the phase separation of the silicate was not observed. In addition, the Hf-silicate films remain amorphous phase.

Key words : Hf-silicate films, High k dielectric, Poly Si, Thermal stability, Integration

1. Introduction

Recently, high k dielectric films have been suggested as alternatives to the currently employed SiO_2 gate dielectric for the Complementary Metal Oxide Semiconductor Field Effect Transistor (CMOS-FET) technology since high k dielectrics reduce the leakage current and improve the reliability without decreasing capacitance of oxide.[1,2] Several binary metal oxides, such as Ta_2O_5, ZrO_2, and HfO_2, have been investigated as an high k gate dielectric films,[3-6] however, binary metal oxide have some problems including relatively low crystallization temperature,[7,8] a large increase of Equivalent Oxide Thickness (EOT) upon high temperature annealing,[8] and boron penetration in P^+ MOS-FET devices.[9] In addition, the heterointerface formed between metal oxide and Si channel degrades the carrier mobility in MOS-FET devices.[10] In order to solve these problems, high k dielectric films should have amorphous phase up to high temperature annealing (>900°C) for the low carrier conduction and boron penetration and have a flat pseudo-homointerface between high k dielectric films and Si substrate for the high mobility.[11-14]

Considering the thermal stability and electrical results, Zr-silicate and Hf-silicate films are suggested as a very promising high k dielectric films due to an amorphous phase and thermal stability in direct contact with Si after annealing at 1050°C for 20 sec.[10] However, a detail chemical investigation on the interfacial reaction between poly Si and Zr silicate or Hf-silicate films during the post process has not been performed.

In this paper, the effects of SiH_4 gas on the surface of Hf-silicate films during the deposition of poly Si films and the thermal stability of sputtered Hf-silicate films in poly Si/Hf-silicate film have been investigated by using HR-TEM and XPS.

2. Experimental Procedure

After the Radio Corporation of American (RCA) method cleaning of the p-type silicon wafer with 3~5 Ωcm, 6 nm thick Hf siliacte films were deposited at Room Temperature (R.T.) by reactive DC magnetron sputtering from a Hf target with 99.9% purity and undoped Si target. The sputtering pressure was 3 mTorr in $Ar+O_2$ gas ambient and both the Hf sputtering power and Si sputtering power are 100 W. As-deposited Hf-silicate was composed of 14% Hf, 20% Si, and 66% O within XPS detection limit and had the rms roughness of 4 Å. After the deposition of Hf-silicate films, poly Si films were grown on Hf-silicate films using a Low Pressure Chemical Vapor Deposition (LPCVD) system.[15] The deposition temperature was 600°C and deposition pressure was maintained at about ~ 340 mTorr with 100% SiH_4 as source gases using auto pressure controller. After the formation of Metal-Oxide-Semiconductor(MOS) structure, the specimens were annealed at 900°C for 30 min in N_2 ambient. Then, the effects of SiH_4 gas on the surface of Hf-silicate films during the deposition of poly Si films and the

†Corresponding author : Sung-Kwan Kang
E-mail : skk@stanford.edu
Tel : 1-650-387-9516 Fax : 1-650-725-4034

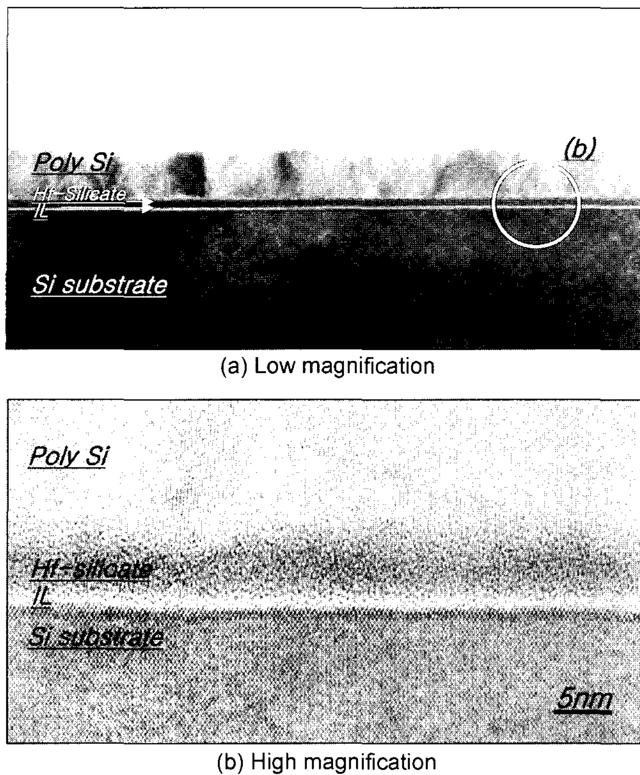


Fig. 1. TEM micrographs of poly Si/Hf-silicate/Si substrate structure after annealing at 900°C in N_2 ambient for 30 min.

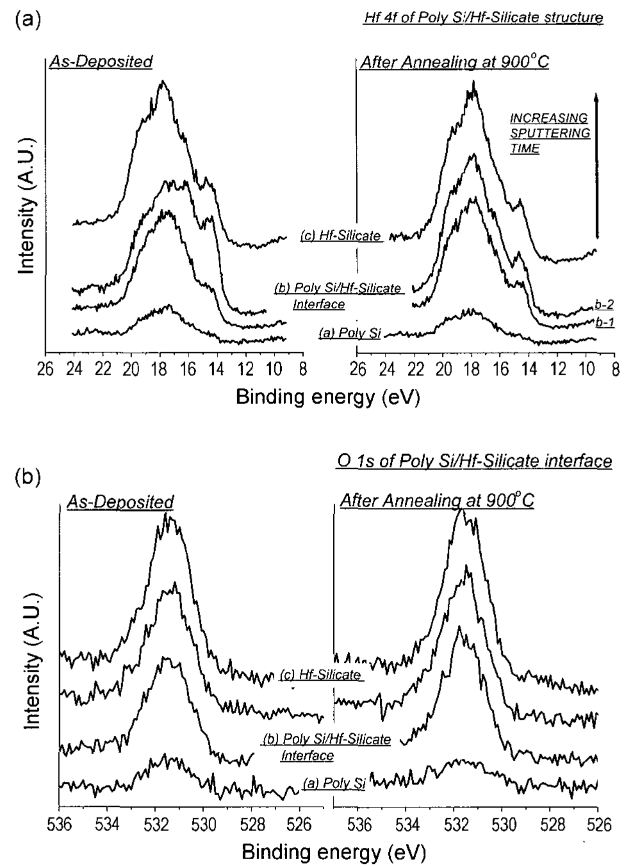


Fig. 2. The XPS depth spectra of (a) Hf 4f and (b) O 1s from poly Si/Hf-silicate interface to Hf-silicate films before and after annealing at 900°C for 30 min.

thermal stability of poly Si/Hf-silicate film was investigated by using HR-TEM and XPS. For the XPS data acquisition, Al Kα radiation was used as photon source and the analysis chamber was maintained at 5×10^{-9} torr. All experimental scans were performed at constant pass energy of 23.5 eV and a constant take off angle of 45°. In addition, the XPS spectra were all taken at room temperature before and after Ar ion sputtering. Ar ion sputtering conditions are ion energy of 3 keV and beam current density of 1.5×10^{-5} A/cm^2.

3. Results and Discussion

Fig. 1 shows HR-TEM micrographs of poly Si/Hf-silicate/Si substrate structure after annealing at 900°C in N_2 ambient for 30 min. Low magnification TEM micrograph shows that Hf-silicate films and Interfacial Layer (IL) has uniform thickness without any notable features. High magnification TEM micrograph shows that while poly Si films have a clear lattice fringe, the Hf-silicate films remain amorphous state after annealing. In addition, the phase separation of the silicate was not observed inside Hf-silicate films and Hf-silicate/IL interface and IL/Si substrate interface are seen to be sharp. However, poly Si/Hf-silicate interface has some roughness, resulted from the reaction between poly Si and Hf-silicate films. Previously, G. D. Wilk *et al.* reported that poly Si/Hf-silicate interface have remained atomically sharp after annealing at 1050°C for 20 sec in contrast to our results. These differences are attributed to the Si film deposition condition. They deposited amorphous Si on the silicate films at 25°C, however, we deposited poly Si films on Hf-silicate films at 600°C using SiH_4 gas. In our system, SiH_4 gas was expected to react with Hf-silicate films easily and new Hf-compound was formed at the poly Si/Hf-silicate interface during the poly Si films deposition due to the high activity of SiH_4 gas at the poly Si deposition temperature.(see the Fig. 2) The interfacial reaction between SiH_4 and Hf-silicate films will be discussed below in XPS results and thermodynamic considerations.

To investigate the chemical state of poly Si/Hf-silicate in detail, XPS analysis was performed. For the XPS analysis, 10 nm thick poly Si/Hf-silicate gate stacks were fabricated and annealed under the same annealing conditions. Initially, 10 nm thick poly Si films were etched to poly Si/Hf-silicate interface by Ar ion sputtering in XPS chamber and then, the spectra of Hf 4f, Si 2p, and O 1s were obtained at each Ar ion sputtering step from the poly Si/Hf-silicate interface to Hf-silicate films. Fig. 2 shows the XPS depth spectra of Hf 4f and O 1s from poly Si/Hf-silicate interface to Hf-silicate films before and after annealing at 900°C for 30 min. In the both the Hf 4f spectra of poly Si/Hf-silicate before and after annealing at 900°C, the spin-orbit splitting

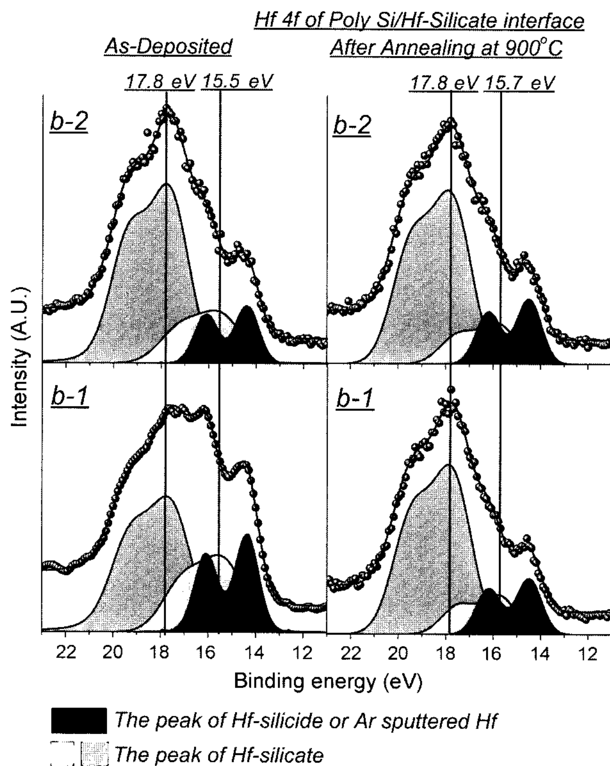
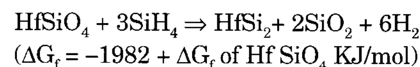


Fig. 3. The deconvoluted XPS spectra of Hf 4f at the poly Si/ Hf-silicate interface before and after annealing at 900°C for 30 min.

between Hf $4f_{7/2}$ and Hf $4f_{5/2}$ was not clearly observed indicating the presence of Hf in multiple oxidation states (see the Fig. 3). In Hf 4f spectra, the peak intensity increased at about 17.8 eV in both as-deposited and annealed 900°C for 30 min, which is indicative of the Hf $4f_{7/2}$ peak position of Hf-silicate. J. J. Chambers *et al.* and G. D. Wilk *et al.* reported that the binding energy of metal for metal silicate, such as yttrium silicate and hafnium silicate, is ~ 1 eV higher than that of metal oxide due to the donation of electron from metal to the Si-O bond in the metal silicate with the relative electronegativities of metal, silicon, and oxygen.[10,16] In addition, the position of highest peak in Hf spectra did not change after annealing at 900°C indicating that the chemical structure, such as phase separation and crystal structure, did not change, as shown in Fig. 1(b). This chemical stability of Hf-silicate was also confirmed from O 1s spectra. Fig. 2(b) shows the XPS depth spectra of O 1s from poly Si/Hf-silicate interface to Hf-silicate films before and after annealing at 900°C for 30 min. After annealing at 900°C for 30 min, no evidence of the change in chemical structure was observed in the poly Si/Hf-silicate system.

To analyze the binding energy of Hf 4f at the poly Si/Hf-silicate interface and the top of the Hf-silicate in detail, we performed the deconvolution of Hf 4f at the poly Si/Hf-silicate interface. Fig. 3 shows the deconvoluted spectra of Hf 4f at the poly Si/Hf-silicate interface after annealing at 900°C for 30 min. In the poly Si/Hf-silicate film before and after annealing at 900°C, the spectra consist of three components at the poly Si/Hf silicate interface : the first one at about 17.8 eV and the second one at about 15.5 eV are the indicative of Hf atoms in Hf-silicate, which are resulted from the presence of Hf in multiple oxidation states, and the third one at about 14.5 eV is predicted to be the spectra of Hf in Hf-silicide or Ar ion sputtered Hf, the peak positions of which are similar. Ar ion sputtered Hf could be observed due to the preferential etching rate, resulting from the difference in atomic mass.[17] Compared with the peak intensity of Hf of 14.5 eV at the as-deposited poly Si/Hf-silicate interface (b-1), that of Hf in Hf-silicate films decreased at 14.5 eV in spite of the increasing Ar ion sputtering time. In addition, the peak intensity of Hf of 14.5 eV increased at the annealed poly Si/Hf-silicate interface under the same Ar ion sputtering conditions with the increase of etching time. From these results, the peak of Hf of 14.5 eV at the as-deposited poly Si/ Hf-silicate interface is predicted to be Hf-silicide, resulting from the reaction between poly Si and the Hf-silicate films.

Why does the Hf-silicide form the poly Si/Hf-silicate during the deposition of poly Si films? The formation of Hf silicide at the poly Si/Hf-silicate interface is due to the reaction between SiH_4 and Hf-silicate films during the poly Si deposition. When SiH_4 gas is streamed in LPCVD system at 600°C, the deposition process occurs from the reaction with SiH_4, silyne (SiH_2) or intermediate silylene. Since SiH_4 has the lowest Gibbs free energy among the three species, we calculated the Gibbs free energy of reaction using the value of SiH_4.[18] In addition, we considered $HfSi_2$ as silicide layer since $HfSi_2$ has the lowest Gibbs free energy per atomic mole among the Hf-silicides.[19] Although we did not know the free energy of Hf-silicate exactly, that of Hf-silicate was expected to be slightly lower than that of $ZrSiO_4$, which is about −1681 KJ/mol at 600°C because Hf-compound are more stable than Zr-compound.[19] From the below reactions, Hf-silicide can be formed on top of the Hf-silicate films during the deposition of poly Si films.



$$HfSiO_4 + 3SiH_4 \Rightarrow HfSi_2 + 2SiO_2 + 6H_2$$
$$(\Delta G_f = -1982 + \Delta G_f \text{ of } HfSiO_4 \text{ KJ/mol})$$

After annealing at 900°C, Hf silicide reacted with SiO_2 again and the reaction formed Hf-silicate on the top of the initial Hf-silicate films without changing the chemical structure of initial Hf-silicate films. Therefore, the peak intensity of Hf silicide at 14.5 eV decreased clearly and that of Hf-silicate at 17.8 eV increased at the poly Si/Hf-silicate interface after annealing at 900°C, as shown in Fig. 2.

Fig. 4 shows the deconvoluted Si 2p spectra of poly Si/Hf-silicate interface before and after annealing at 900°C. In Si 2p spectra, the spectra consist of three components at the poly Si/Hf silicate interface : the first one at about 102 eV and the second one at about 100.3 are the indicative of Si atoms in Hf-silicate, which are resulted from the presence of Si in multiple oxidation states, like Hf 4f spectra and the third one at about 99.2 eV is predicted to be the spectra of Si atoms in poly Si including Si atoms in Hf-silicide. While the

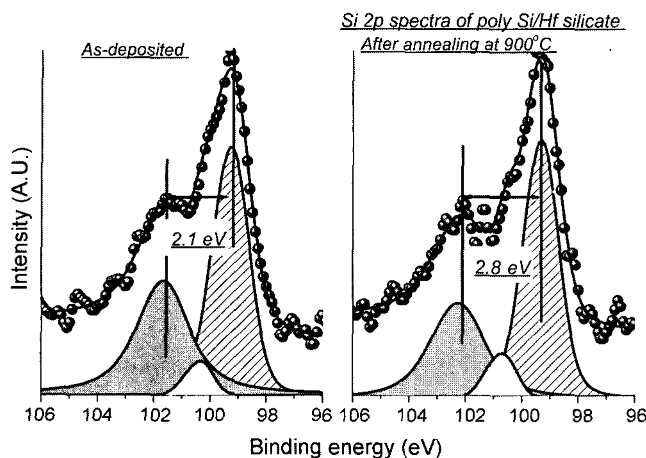


Fig. 4. The XPS spectra of Si 2p at the poly Si/Hf-silicate interface before and after annealing at 900°C for 30 min.

energy separation between the peak of poly Si and that of SiO_x is 2.1 eV in as-deposited poly Si/Hf-silicate system, the energy separation between the peak of poly Si and that of SiO_x increased to 2.8 eV, which is typical energy separation between Si and metal silicate, in annealed poly Si/Hf-silicate system. These results mean that intermediate bonding states of Si with lower binding energy than that of silicate changed to the binding state of silicate after annealing. That is, the number of Si atoms bonding to Hf atoms at the nearest neighbor decreased and the number of Si atoms boning to O atoms increased due to the formation of Hf-silicate at the poly Si/Hf-silicate interface, indicating that Hf silcide disappeared at the poly Si/Hf silicate interface as shown in Hf 4f spectra (Fig. 2).

4. Conclusions

We investigated the effects of SiH_4 gas on the surface of Hf-silicate films during the deposition of poly Si films and the thermal stability of sputtered Hf-silicate films in poly Si/Hf-silicate system before and after annealing by using HR-TEM and XPS. After poly Si film deposition at 600°C, Hf silicide was formed at the poly Si/Hf-silicate interface due to the reaction between active SiH_4 gas and Hf-silicate films. The formation of Hf silicide was observed using Hf spectra and Si spectra of XPS data. After annealing at 900°C, the phase separation of the silicate was not observed and the chemical structure of Hf-silicate films was not changed. However, poly Si/Hf-silicate interface has some roughness since newly formed Hf silicide changed to Hf-silicate during the annealing.

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