Thermal stability of HfTaON films prepared by physical vapor deposition*

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Abstract: We investigate the thermal stability of HfTaON films prepared by physical vapor deposition using high resolution transmission electronic microscope (HRTEM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the magnetron-sputtered HfTaON films on Si substrate are not stable during the post-deposition annealing (PDA). HfTaON will react with Si and form the interfacial layer at the interface between HfTaON and Si substrate. Hf–N bonds are not stale at high temperature and easily replaced by oxygen, resulting in significant loss of nitrogen from the bulk film. SiO_2 buffer layer introduction at the interface of HfTaON and Si substrate may effectively suppress their reaction and control the formation of thicker interfacial layer. But SiO_2 is a low *k* gate dielectric and too thicker SiO_2 buffer layer will increase the gate dielectric's equivalent oxide thickness. SiON prepared by oxidation of N-implanted Si substrate has thinner physical thickness than SiO_2 and is helpful to reduce the gate dielectric's equivalent oxide thickness.

Key words: HfTaON; physical vapor deposition; thermal stability; interfacial layer

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1. Introduction

As the continuous scale down of complementary metal–oxide–semiconductor field effect transistor, traditional gate dielectrics of SiO_2 or SiON cannot meet the requirement of high speed and low power due to large direct tunneling leakage. In order to overcome these issues, much effort has been made to develop alternative materials. High dielectric constant (high *k*) materials, as a replacement for conventional gate dielectrics, have attracted attention in the past few years because of their potential for reducing gate leakage current while keeping the equivalent oxide thickness (EOT) thin[1, 2].

HfO_2 is considered as one of the most promising high-*k* gate dielectrics for its reasonable *k* value (about 25), the relatively large band gap (5.68 eV), and the thermodynamic compatibility with Si[3, 4]. However, it crystallizes readily by low-temperature annealing around 400–600 °C. HfTaO emerges as a candidate for improvement of the crystallization temperature due to the Ta atom distribution in the film[5]. In order to maintain the thermal stability, a nitrogen passivation is one of the powerful techniques used for high-*k* material fabrication. Yu *et al.* reported that HfTaON is one of the most desirable materials for the next-generation device applications due to its ability to retain the amorphous structure through high temperature thermal annealing processes for activation[6]. Unfortunately, like other Hf-based high *k* gate dielectrics, HfTaON easily reacts with Si substrate and thus an undesired low-*k* interfacial layer is formed. The fundamental understanding of the HfTaON/Si interface is important because many issues, such as thermal and chemical stability, electrical performance and interface charge density, are related to the interface chemical state. In this paper, we investigate the interfacial structure of HfTaON on Si substrate using HRTEM and XPS analysis. SiO_2 or SiON buffer layer is introduced at the interface between HfTaON and Si substrate to resolve this problem.

2. Fabrication

After a standard cleaning process, Si wafer was treated with a HF/IPA/H_2O solution to prevent the deposition of particle, metal ion and organic contamination, as well as to suppress the growth of nature oxide[7]. HfTaON films were deposited on the wafer with or without a buffer layer by magnetron sputtering using Hf and Ta targets at room temperature in Ar/N_2 mixture. The Hf and Ta contents in the films were controlled by adjusting Hf and Ta sputtering power and time. After deposition, the post deposition annealing (PDA) was performed at 700 and 1000 °C for 10 s, respectively. HfTaON films were analyzed by high resolution transmission electronic micrograph (HRTEM). The chemical composition and bonding states of films were investigated by the XPS analysis with a monochromatic Al Kα (1486.6 eV) X-ray incident. The binding energy (BE) was referenced to C1s at 284.5 eV.

3. Results and discussion

Figure 1 shows the annealing-temperature dependence of HRTEM images for HfTaON deposited on Si substrate. The films still retain amorphous after 1000 °C PDA, which indicates that Ta incorporation into HfON film can improve its crystallization temperature. There forms an interfacial layer, whose thickness is sensitive to the annealing temperature,

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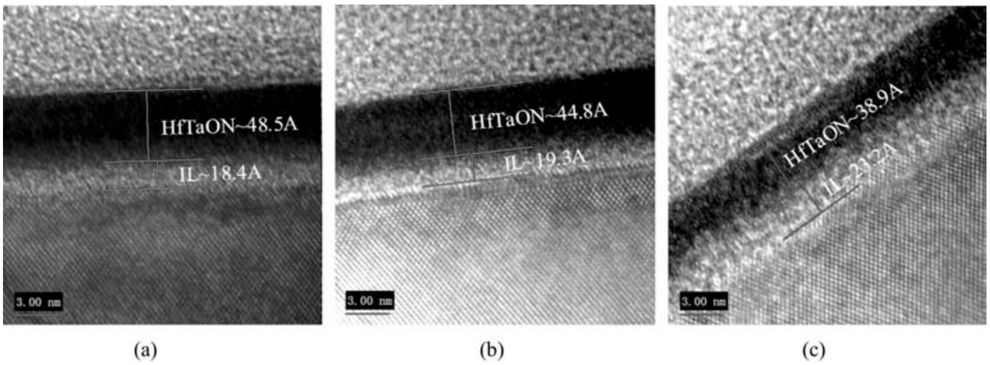


Fig.1. HRTEM images of HfTaON on Si substrate: (a) As deposition; (b) 700 °C PDA; (c) 1000 °C PDA.

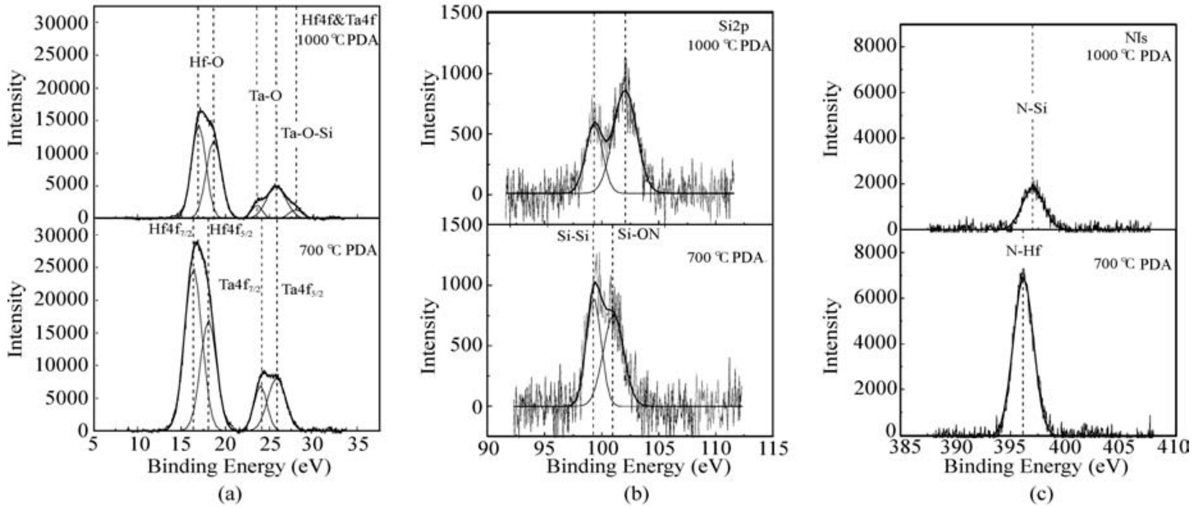


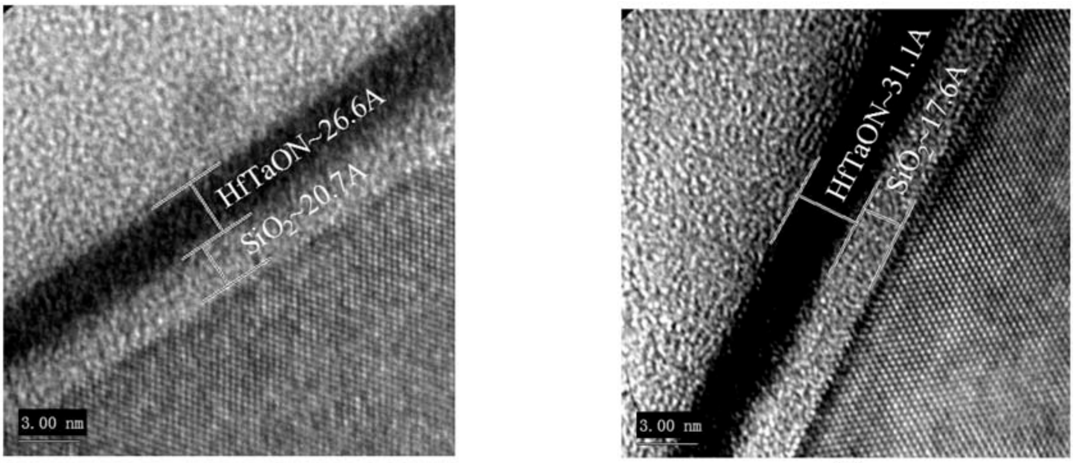
Fig.2. XPS spectra of HfTaON on Si after 700 and 1000 °C PDA: (a) Hf4f and Ta4f; (b) Si2p; (c) N1s.

between HfTaON film and Si substrate. As deposition, the thickness of the interfacial layer is 18.4 Å and the interface is rough. After 700 °C annealing, the thickness increases to 19.3 Å and the interface becomes smooth. When the annealing temperature increases to 1000 °C, the thickness becomes 23.2 Å and the interface is rough again. As the thickness of the interfacial layer increases, the thickness of HfTaON films decrease. These results indicate that a chemical reaction happened at the interface between HfTaON film and Si substrate during the post annealing process.

Figure 2 shows the annealing-temperature dependence of Hf4f, Ta4f, Si2p and N1s photoemission spectra of HfTaON films. For the sample annealed at 700 °C, the Hf4f spectrum can be deconvoluted as two peaks, a $Hf4f_{7/2}$ peak at a binding energy of 16.5 eV and a $Hf4f_{5/2}$ peak at a binding energy of 18.3 eV, both of which correspond to the Hf–O bonds[8]. There is no Hf–Si peak existing, which is located at 14.2 eV[9]. These indicate that Hf atoms are only bonded to O atoms as nearest neighbors. For the sample annealed at 1000 °C, the binding energy of $Hf4f_{7/2}$ shifts from 16.5 to 17.1 eV and $Hf4f_{5/2}$ shifts from 18.3 to 18.9 eV. And, the intensity of Hf4f spectrum is reduced significantly. These indicate that Hf silicates are formed at the interface, according to Wilk's results that the binding energy of $Hf4f_{7/2}$ peak of Hf silicate is ~1 eV higher than that of HfO_2[10]. Like Hf4f spectrum, the peak intensity of Ta4f spectrum is reduced at 1000 °C. However, an additional intense peak at 28.2 eV appears in the Ta4f spectrum, which corresponds to the Ta–O–Si bond[11, 12]. These indicate that Ta silicates are also formed at the interface.

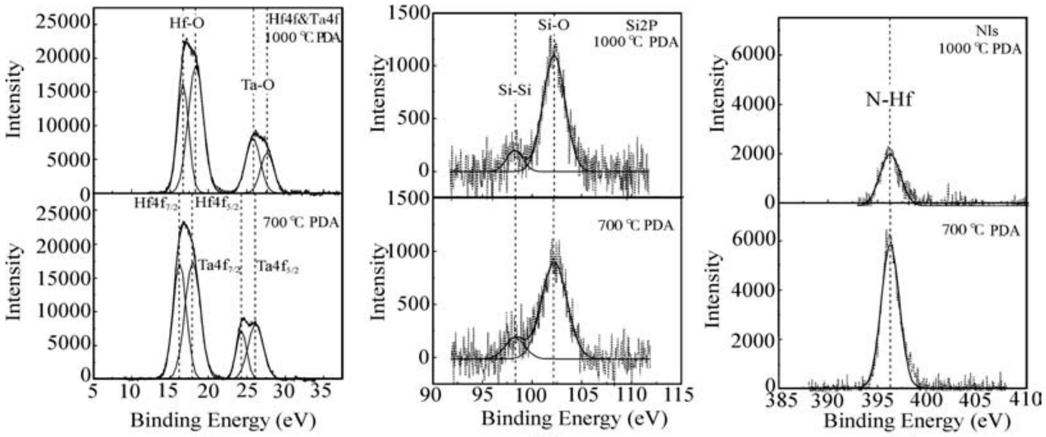
Figure 2 (b) shows the annealing-temperature dependence of Si2p photoemission spectra. The Si2p spectrum annealed at 700 °C can be deconvoluted as two peaks, corresponding to Si substrate (99.3 eV) and the interfacial layer(101–102 eV) respectively. Si bonded to oxygen in a pure SiO_2 layer is located at ~103 eV[13]. The difference between binding energies of the interfacial layer and Si–O bond indicates that the composition of interfacial layer is a silicate-like compound. As the annealing temperature increases from 700 to 1000 °C, the binding energy of the interfacial layer increases from 101 to 102 eV. The binding energy shift in higher direction indicates that more oxygen atoms pass through the high k dielectric and react with Si substrate, forming thicker O-rich interfacial layer.

Figure 2 (c) shows the annealing-temperature dependence of N 1s photoemission spectra. As the annealing temperature increases from 700 to 1000 °C, the intensity of N1s spectrum decreases clearly and its peak moves from 396.1 to 397 eV. This is because that the Hf–N bonds are unstable during the post-deposition annealing and easily substituted by oxygen, resulting in significant loss of nitrogen from the bulk film. The N1s peaks at 396.1 and 397 eV correspond to N–Hf(Ta) and N–Si bonds, respectively[14,15]. The N1s peak shift in direction to higher binding energy indicates that most of remaining N atoms are located at the HfTaON/Si interface



(a) (b)

Fig.3. HRTEM images of HfTaON/SiO_2/Si systems: (a) As deposition; (b)700 °C PDA.



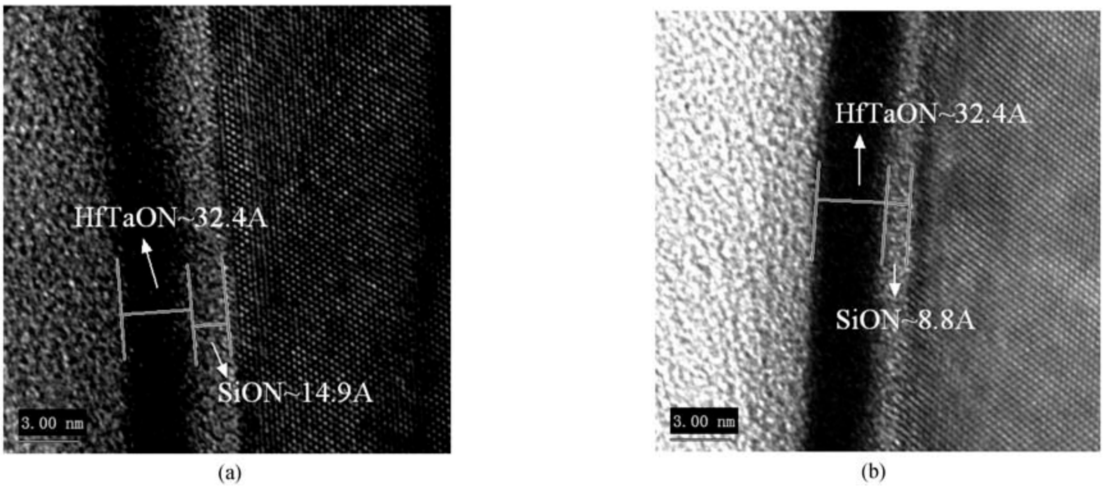
(a) (b) (c)

Fig.4. XPS spectra for HfTaON on SiO_2 after 700 and 1000 °C PDA: (a) Hf4f and Ta4f; (b) Si2p; (c) N1s.

and formed Si–N bonds. These are consistent with the previous paper reported by Kang *et al.*[16].

Based on the above analysis, we can see that HfTaON on Si substrate is not thermally stable and an interfacial layer is usually formed at the interface. The structure of the interfacial layer is complex. As deposition, the sputtering process may activate the Si substrate surface and produce some Si hanging bonds. Hf, Ta, N and O atoms easily react with Si substrate, forming Hf–Si, Ta–Si, N–Si and O–Si bonds. The interfacial layer is a complex mixture of silicides, silicates, SiO_xN_y and so on. Annealing at high temperature will enhance the interdiffusion of Hf, Ta, O, N and Si atoms, changing the interfacial structure. During the 700 °C annealing process, the oxygen atoms pass through the high k layer and react with Si substrate, forming SiO_x interfacial layer. Hf–Si and Ta–Si bonds are changed into Hf–O–Si and Ta–O–Si bonds. The interfacial structure changes into the mixture of silicates and SiO_xN_y. During the 1000 °C annealing process, the interdiffusion of Hf, Ta, O, N and Si atoms becomes more active. More oxygen atoms pass through the high k layer and react with Si substrate. Many silicon atoms diffuse into HfTaON film, forming more Hf silicates and Ta silicates. Hf and Ta atoms diffuse into the interfacial layer, making HfTaON film thinner. Oxygen diffusion through high k layer is fast, silicon diffusion is secondary while Hf and Ta diffusion is slowest and weakest[17]. So, Hf silicates and Ta silicates are dominating at the upper part of the interfacial layer. Moving lower, SiO_xN_y content will increase.

In order to suppress the interdiffusion of Hf, Ta, O, N and Si atoms, SiO_2 buffer layer is introduced at the interface between HfTaON and Si substrate, as shown in Fig.3. Comparing the samples as-deposited and annealed at 700 °C, SiO_2 buffer layer decreases from 20.7 to 15.8 Å while the HfTaON layer increases from 26.6 to 31.1 Å, which indicate that the chemical reaction happens between the HfTaON film and SiO_2 buffer layer. Figure 4 shows the Hf4f and Ta4f XPS spectra for HfTaON on SiO_2 after 700 and 1000 °C PDA processing. As the annealing temperature increases from 700 to 1000 °C, the bonding energy of $Hf4f_{7/2}$ shifts from 16.3 to 16.7 eV and $Hf4f_{5/2}$ shifts from 17.9 to 18.3 eV. Comparing with HfTaON on a Si substrate, a smaller shift can be obtained, which indicates that the SiO_2 buffer layer is helpful to suppress Hf silicate formation. At the same time, the bonding energy of $Ta4f_{7/2}$ shifts from 24.3 to 25.8 eV and $Ta4f_{5/2}$ shifts from 26.1 to 27.6 eV. A sizable shift of about 1.5 eV is obtained, which indicates that Ta oxide has reaction with the SiO_2 buffer layer and many Ta silicates are produced. Figure 4 (b) shows the Si2p XPS spectra for HfTaON on SiO_2 after 700 and 1000 °C PDA processing. The two peaks correspond to Si substrate



(a) (b)

Fig.5 HRTEM images of HfTaON/SiON/Si systems: (a) As deposition; (b) 700 °C PDA.

and SiO_2 buffer layer. There is no change of Si2p XPS spectrum except that the intensity of Si peak increases appreciably after 1000 °C PDA processing. This indicates that the SiO_2 buffer layer is helpful to suppress O atom diffusion into Si substrate and reduce SiO_x interfacial layer formation. Figure 4 (c) shows the N1s XPS spectra for HfTaON on SiO_2 after 700 and 1000 °C PDA processing. After 1000 °C PDA processing, the intensity of N1s spectrum decreases clearly and its binding energy shows no change. This indicates that SiO_2 buffer layer is helpful to prevent N atoms from diffusing into Si substrate and forming Si–N bonds. The study results indicate that SiO_2 buffer layer introduction at the interface of HfTaON and Si substrate can suppress the inter-diffusion of Hf, Ta, O, N and Si atoms, which is helpful to limit thicker interfacial layer formation.

But, SiO_2 is a low k gate dielectric and too thick a SiO_2 buffer layer will increase the gate dielectric's equivalent oxide thickness. In order to control the thickness of SiO_2 buffer layer, an ultrathin SiON buffer layer is prepared by oxidation of N-implanted Si substrate at the interface between HfTaON film and Si substrate[7]. Before the SiO_2 buffer layer formation, nitrogen was implanted into silicon substrate with a dosage of 4.5×10^{14} cm^{-2} through the screen oxide. Nitrogen can reduce the oxidation rate, and the reduction of oxidation rate increases with the nitrogen dose greatly. Si–N bond has lower binding energy than Si–O bond. During annealing at high temperature, the chemical reaction at the interface of HfTaON on SiON is more active than HfTaON on SiO_2, which making more SiON buffer layer to be consumed, resulting in thinner interfacial layer. Both of these are helpful to reduce the gate dielectric's equivalent oxide thickness. Figure 5 shows the HRTEM images of HfTaON/SiON/Si systems. The thickness of SiON buffer layer is 14.9 Å as deposition and 8.8 Å for annealing at 700 °C, respectively. Figure 6 shows the high-frequency C–V curves of HfTaON/SiO_2 and HfTaON/SiON gate dielectrics annealed at 900 °C. Compared capacitances in accumulation of the two samples, we find that the capacitance of HfTaON/SiON gate dielectric is higher than HfTaON/SiO_2 gate dielectric, which indicates that HfTaON/SiON gate dielectric has thinner EOT than HfTaON/SiO_2 gate dielectric.

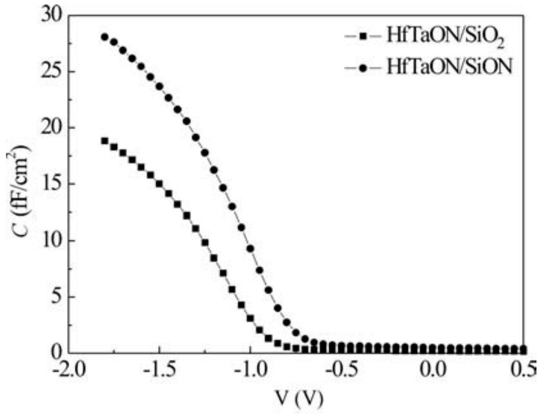


Fig.6. High-frequency C–V curves of HfTaON/SiO_2 and HfTaON/SiON gate dielectrics annealed at 900 °C.

4. Conclusion

In summary, we have investigated the thermal stability of HfTaON prepared by magnetron sputtering on Si substrate, SiO_2 and SiON respectively. The results indicate that HfTaON gate dielectric has higher crystallization temperature, retaining amorphous under 1000 °C temperature. Like other Hf-based high k gate dielectrics, there is also an interfacial layer formed between HfTaON film and Si substrate. Its formation is because of the interdiffusion of Hf, Ta, O, N and Si atoms. The interfacial structure is sensitive to the annealing temperature. Annealing at higher temperature will enhance the interdiffusion of Hf, Ta, O, N and Si atoms and forming thicker interfacial layer. Hf(Ta) silicates and SiO_xN_y species are the main body of the interfacial layer. SiO_2 buffer layer introduction at the interface of HfTaON and Si substrate may effectively suppress the atoms' interdiffusion and limit the interfacial layer formation. But, SiO_2 is a low k gate dielectric and too thicker SiO_2 buffer layer will increase the gate dielectric's equivalent oxide thickness. In order to reduce the gate dielectric's equivalent oxide thickness, SiON buffer layer is prepared by oxidation of N-implanted Si substrate to substitute SiO_2 buffer layer, thinner interfacial layer is obtained.

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