Phase separation and interfacial reaction of high-*k* HfAlO$_x$ films prepared by pulsed-laser deposition in oxygen-deficient ambient

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Ultrathin high-*k* HfAlO$_x$ films on silicon wafers are prepared by pulsed-laser deposition in oxygen-defective ambient. The precipitation of HfO$_x$ clusters from HfAlO$_x$ matrix is revealed by x-ray photoelectron spectroscopy. It is argued that the HfO$_x$ clusters react with silicon to form Hf-silicide interfacial layer at a temperature as low as 600 °C, which evolves into Hf-silicate in the subsequent postannealing at 700 °C for 30 s in oxygen ambient. The optimized fabrication conditions developed to avoid the formation of interfacial layer is employed to prepare high-quality HfAlO$_x$ films of excellent electrical characteristics, such as a dielectric constant of 17.7, a small equivalent oxide thickness of 0.66 nm, a flatband voltage of 0.45 V, and a low leakage current density of 53.8 mA/cm^2 at 1 V gate voltage. © *2006 American Institute of Physics*.
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The continued downsizing of Si complementary metal-oxide-semiconductor (MOS) devices has led to the inevitable need of replacing SiO$_2$ gate insulator with high-*k* dielectric oxides in order to maintain a smaller leakage current without losing gate control of the channel region.[1] Among many candidates, ZrO$_2$ (see Ref. 2) and HfO$_2$ (see Ref. 3) have been highlighted due to their high permittivity and good thermodynamic stability in contact with the Si, but their crystallization temperature is low (400–500 °C). Zr(Hf)-silicate (aluminate), however, obtains a high crystallization temperature of 800–1000 °C with sacrificing the effective dielectric by incorporating low dielectric constant SiO$_2$(Al$_2$O$_3$) into ZrO$_2$(HfO$_2$).[4–7]

Previous reports[8–10] often revealed the existence of interfacial layers of silicon oxide, silicate, or silicide between high-*k* films and Si substrates during the deposition/annealing process. These products from the interfacial reaction suppress the effective dielectric constant and degrade the electrical performances of devices. A careful characterization of the interfacial microstructure and chemistry at atomic scale becomes necessary for any potential high-*k* dielectrics.

Furthermore, for single-element oxide (M_xO_y), the interface reaction between metal/oxygen ions and Si results in the interfacial layer.[11,12] However, for pseudobinary alloy (M_xO_y–SiO$_2$ or M_xO_y–Al$_2$O$_3$, where M=Zr,Hf, etc.), it seems that nanoscale phase separation becomes inevitable upon deposition/annealing at relatively high temperature. Quevedo-Lopez *et al.*[13] contributed the formation of the interfacial layer to the interfacial reaction between incorporated Zr(Hf) ions and Si, while it was demonstrated by Kim *et al.*[14] that the phase separation of the metal silicate films rather than the interfacial reaction results in a SiO$_2$-rich silicate interface layer. Additionally, Quevedo-Lopez *et al.*[15]

recently confirmed that the SiO$_2$ interfacial layer is the result of both interfacial reactions and phase separation of metal-silicate at high temperature. In this letter, we investigate the interfacial microstructure of HfAlO$_x$ films deposited in oxygen-deficient ambient. A phase separation of amorphous HfAlO$_x$ into HfO$_x$ clusters is indeed identified, which assists subsequent interfacial reactions between HfO$_x$ and Si, resulting in formation of Hf-silicide interfacial layer at a temperature as low as 600 °C.

The Hf-aluminate ceramic target was obtained by sintering a cold-pressed mixed powder pellet (1:1 mole rate of HfO$_2$ and Al$_2$O$_3$) at 1500 °C for 6 h. The *n*-type Si(100) substrates were etched in diluted hydrofluoric solution (1:25 HF:H$_2$O) for 2 min to remove the native SiO$_2$ layer and leave an H-terminated Si surface. Ultrathin HfAlO$_x$ films of a few nanometers in thickness were deposited at T_s=500, 600, 700, and 800 °C in oxygen partial pressure of ∼10^{-5} Pa ambient using a KrF excimer laser ablation system (COMPEX 201, Lambda Physik AG, 248 nm in wavelength, 30 ns in pulsed width) running at a repeat of 5 Hz with an average energy density of ∼1 J/cm^2. Some samples containing Hf-silicide (to be revealed subsequently) were annealed in oxygen ambient at 600 and 700 °C for 30 s, respectively. High-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS, ESCALAB MK2) were used to investigate the microstructure and chemistry of HfAlO$_x$ films. The capacitance-voltage (*C*-*V*) characteristics of Pt/HfAlO$_x$/*n*-Si MOS structures were measured using an Aglient 4294A precision impendence analyzer.

The x-ray diffraction revealed that the HfAlO$_x$ films deposited at $T_s \leqslant 800$ °C were amorphous. However, the films deposited at $T_s > 500$ °C showed relatively poor electrical performance, which predicts possible existence of interfacial layer or inhomogeneity in the films. This stimulated us to investigate carefully the interfacial structure of the as-prepared HfAlO$_x$ films using XPS. Before loaded into the photoemission chamber, the top layers of all samples were

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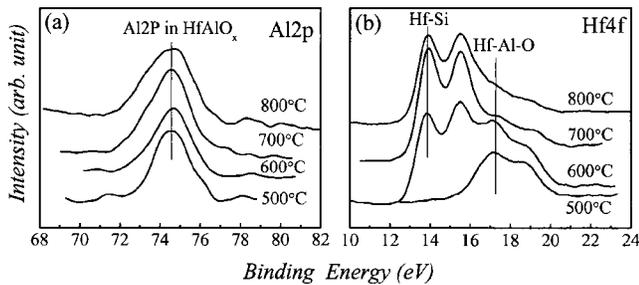[a)]Author to whom correspondence should be addressed; electronic mail: liujm@nju.edu.cn

FIG. 1. XPS spectra of (a) Al 2*p* and (b) Hf 4*f* core levels for as-deposited HfAlO$_x$ films deposited in oxygen partial pressure of $\sim 10^{-5}$ Pa ambient at 500, 600, 700 and 800 °C, respectively.
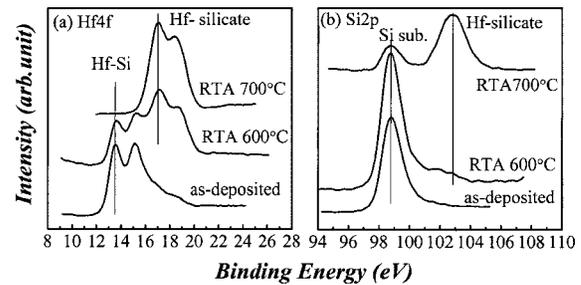

FIG. 2. XPS spectra of (a) Hf 4*f* and (b) Si 2*p* core levels for HfAlO$_x$ films deposited at 800 °C in oxygen partial pressure of $\sim 10^{-5}$ Pa and rapidly thermally annealed in oxygen ambient at 600 and 700 °C for 30 s, respectively.

etched using Ar ion beam in order to reach the regions very close to the HfAlO$_x$/Si interface. The collected data were corrected for charging effect-induced peak shifts using the binding energy of adventitious carbon C 1*s* peak (284.6 eV). The evaluated XPS spectra for Al 2*p* and Hf 4*f* core levels are shown in Fig. 1. It was observed that for different T_s, the Al 2*p* peak remains stationary, while the Hf 4*f* reflection changes a lot with increasing T_s, as shown as Figs. 1(a) and 1(b) respectively. At T_s=500 °C, only a doublet peak corresponding to the Hf–Al–O bond[16] was observed, while a new doublet peak corresponding to the Hf–Si bond[17] appeared at T_s=600 °C. The peak from the Hf–Al–O bond fell with increasing T_s and finally disappeared at T_s=800 °C. In contrast to this, the peak intensity from Hf–Si bond was enhanced significantly with increasing T_s. No shift of the Al 2*p* peak and decaying of the Hf 4*f* doublet peak (Hf–Al–O) upon increasing T_s allow us to argue that HfO$_x$ clusters precipitated from amorphous HfAlO$_x$ at T_s=600 °C and above. These XPS results demonstrate the phase separation of HfAlO$_x$ under the deposition conditions just described.

Moreover, the emergence of Hf 4*f* doublet peak (Hf–Si) indicated that the HfO$_x$ clusters reacted subsequently with Si to form Hf-silicide in oxygen-deficient ambient. At even higher T_s, the reaction of HfO$_x$ clusters with Si to form Hf-silicide is preferred, so that only the Hf 4*f* doublet peak (Hf–Si) left at T_s=800 °C. Unfortunately, it is not possible to distinguish the Si 2*p* level of the Hf–Si bond from the signals of Si substrate because it is very close to the strong Si substrate peak located at ~ 98.8 eV (not presented here). In fact, metal-silicide formed by the reaction between Zr/Hf metal ions and Si at a temperature as low as 200–500 °C was reported,[12,18] but no metal-silicide could be formed by a reaction between ZrO$_2$/HfO$_2$ and Si unless at a temperature as high as 700 °C.[17,19] In the present work, Hf silicide phase at the interface was observed at a temperature as low as 600 °C, because the formation of Hf-silicide at the interface was essentially enhanced by precipitation of HfO$_x$ clusters from HfAlO$_x$. In short, the interfacial reaction taken place for the present system may be divided as two steps: (1) firstly, HfO$_x$ clusters precipitates from HfAlO$_x$ layer at 600 °C and above; and then (2) the HfO$_x$ clusters reacted with Si to form Hf-silicide interfacial layer in heavily oxygen-deficient ambient. Step (1) is not only necessary for step (2), but also enhances the kinetics of step (2), because the HfO$_x$ clusters are nonstoichiometric and more active than HfO$_2$ to react with Si atoms. Referring to Hubbard *et al.*,[20] the following reactions between HfO$_2$ and Si at 700 °C take place:

$$HfO_2 + Si \rightarrow HfSi_z + SiO_2, \qquad (1)$$

$$HfO_2 + Si \rightarrow HfSi_z + HfSi_xO_y. \qquad (2)$$

Additionally, a reaction between HfO$_2$ and poly-Si at 700 °C in ultrahigh vacuum was also confirmed:[17]

$$HfO_2 + 4Si \rightarrow HfSi_2 + 2SiO\uparrow \quad (\Delta G = -46 \text{ kJ/mol}). \quad (3)$$

In our experiments, neither the Si 2*p* peak of SiO$_2$ nor the Si 2*p* peak of silicate was observed; it is thus reasonable to argue that the interfacial reaction between HfO$_x$ and Si in heavily oxygen-deficient ambient takes place following reaction (3). Here it should be emphasized that no Si 2*p* peak of SiO can be observed since it is volatile.

The interfacial Hf-silicide layer is very harmful for electrical performance of HfAlO$_x$ as high-*k* dielectrics. It was reported that the Hf silicide can be directly oxidized to Hf-silicate by postannealing in N$_2$ ambient at 600 °C for 10 s.[21] To check this result, we performed 30 s long postannealing of two HfAlO$_x$ film samples deposited at T_s=800 °C in O$_2$ ambient at 600 and 700 °C, respectively. Corresponding Hf 4*f* and Si 2*p* core-level XPS spectra are presented in Figs. 2(a) and 2(b), respectively. For the sample annealed at 600 °C, the doublet Hf 4*f* peak from Hf-silicate bond was indeed observed, but the doublet peak from Hf–Si bond remained unless the annealing temperature was 700 °C and above. On the other hand, a weak broad Si 2*p* level (~ 102.7 eV) from the silicate was observed at 600 °C, which became the strongest peak by annealing at 700 °C. These data demonstrate that the Hf-silicide interfacial layer can be fully oxidized into Hf-silicate by postannealing of the as-prepared samples at 700 °C for 30 s, while stoichiometric Hf-silicate is good high-*k* dielectric as well.

Based on our investigation, we deposited the HfAlO$_x$ films at T_s=500 °C in oxygen partial pressure of $\sim 10^{-5}$ Pa to suppress the phase separation of HfAlO$_x$, which was demonstrated to take place at $T_s \geqslant 600$ °C, as shown by the XPS spectra in Fig. 1. We also obtained the cross-sectional HR-TEM image of the HfAlO$_x$ film deposited at T_s=500 °C, as shown in Fig. 3. The HfAlO$_x$ prepared under this condition was amorphous and no visible interfacial layer was observed. This represents the optimized deposition condition for HfAlO$_x$ film deposition for high-*k* dielectric gate application. Figure 4 shows capacitance-voltage (*C-V*) and leakage current density-voltage (*J-V*) characteristics of Pt/HfAlO$_x$/Si MOS structure with ~ 3 nm HfAlO$_x$ films prepared under this condition. The actual frequency independence capacitance is calculated from the *C-V* data measured at two high frequencies (f_1=500 kHz and f_2=1 MHz) using the method proposed by Yang and Hu.[22] A small equivalent oxide thick-
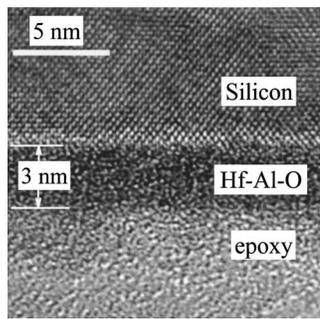
FIG. 3. High-resolution TEM images of HfAlO$_x$ film deposited at 500 °C in oxygen partial pressure of ~10^{-5} Pa ambient. The film is amorphous and has a clean HfAlO$_x$/Si interface.

ness (EOT) of 0.66 nm and a small flatband voltage (V_{fb}) of 0.45 V are estimated from the accumulation capacitance without accounting for quantum mechanical effects. Moreover, because of no interfacial layer, the dielectric constant ~17.7 can be estimated from EOT by the standard procedure.[1] It is noted that the accumulation capacitance has a slight decrease when the gate voltage is above 1 V. A similar phenomenon was also observed by Wang *et al.*.[23] Henson *et al.*[24] discussed this phenomenon qualitatively, and attributed this decrease of capacitance in the accumulation region to the gate current and series resistance. In our experiment, the HfAlO$_x$ film is as thin as ~3 nm. We may reasonably argue that the tunneling conductance of the gate oxide may be large when the gate voltage is above 1 V. Therefore, the capacitance in the accumulation region would show a slight decrease upon increasing gate voltage. In additionally, as shown as the inset in Fig. 4, a leakage current density (J) of 53.8 mA/cm^2 at 1 V gate voltage was obtained, which is much smaller than that of SiO$_2$ films with the same EOT. Chon *et al.*[16] reported that ~3 nm thick N-incorporated HfAlO$_x$ films fabricated by atomic layer deposition has a low leakage density of ~10 mA/cm^2 at −1 V gate voltage. They attributed this excellent leakage characteristic to the increase of the interfacial barrier due to N-atom incorporation. In our experiment, the obtained HfAlO$_x$ film is amorphous, homogeneous, and has a high dielectric constant (~17.7). Moreover, the most noticeable improvement is that the ordinary interfacial layer, which is usually non-stoichiometric and full of defects and interfacial traps, is completely suppressed under the optimized fabrication conditions. This improvement
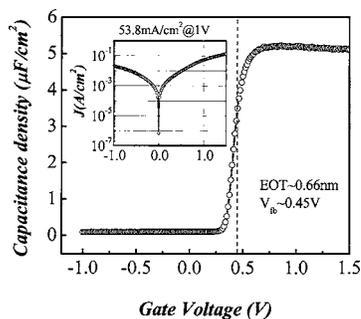
of interfacial characteristics is responsible for the low gate leakage.

In conclusion, we have investigated the phase separation and interfacial reaction of ultrathin amorphous HfAlO$_x$ films deposited on silicon substrates by pulsed-laser deposition in oxygen-defective ambient. For the sample deposited at 600 °C and above, precipitation of HfO$_x$ clusters from HfAlO$_x$ and subsequent reaction between the HfO$_x$ clusters and Si to form Hf-silicide interfacial layer have been found. This Hf-silicide layer can be fully oxidized into Hf-silicate after a postannealing of the sample at 700 °C for 30 s in oxygen ambient. Under the optimized deposition condition the amorphous HfAlO$_x$ film with clean HfAlO$_x$/Si interface has been prepared, which exhibits excellent electrical performance evidenced by a dielectric distance of 17.7, a small EOT=0.66 nm, a narrow flatband voltage V_{fb}=0.45 V and leakage current density J=53.8 mA/cm^2 at 1 V gate.

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FIG. 4. Capacitance density (C_{acc}/A) and leakage current density (J) (inset) as a function of voltage (V) for Pt/HfAlO$_x$/n-Si capacitor with ~3 nm HfAlO$_x$ films deposited at 500 °C in oxygen partial pressure of ~10^{-5} Pa. Dashed line is the position of zero flatband voltage.