Study of interfacial reaction and its impact on electric properties of Hf–Al–O high-*k* gate dielectric thin films grown on Si

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Amorphous thin films of Hf–Al–O (with atomic ratio of Al/Hf of about 1.4) were deposited on (100) *p*-Si substrates by pulsed-laser deposition using a HfO_2 and Al_2O_3 composite target. Transmission electron microscopy was employed for a detailed study of the interfacial reaction between the Hf–Al–O films and the Si substrates. Islands of Hf silicide formed from interfacial reaction were observed on the surface of the Si substrate. The formation of Hf silicide is attributed to the presence of Al oxide in the films that triggers the reaction between Hf atoms in the amorphous Hf–Al–O films and Si under an oxygen deficient condition. The impact of silicide formation on the electrical properties was revealed by high-frequency capacitance–voltage (C–V) measurements on metal–oxide–semiconductor capacitors. The observed abnormal C–V curve due to interfacial reaction was discussed. © *2003 American Institute of Physics.*
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Many high-*k* materials are currently being considered as potential replacements for SiO_2 for gate dielectrics in the future complementary metal–oxide–semiconductor (CMOS) technology.[1–8] Among them, HfO_2 and ZrO_2 as well as their silicates are attractive candidates due to their thermal stability when in contact with Si.[4–6] HfO_2 and ZrO_2 are expected to be thermodynamically stable with the Si substrate based on Gibbs free energy analysis under equilibrium conditions.[9,10] In practice, however, during film deposition or the high temperature annealing process, interfacial reactions have been observed at HfO_2/Si and ZrO_2/Si interfaces. Several authors have reported the formation of $ZrSi_2$ in the ZrO_2/Si interface under ultrahigh vacuum annealing due to oxygen deficiency.[11,12] On the other hand, it is well known that HfO_2 and ZrO_2 are poor barriers to oxygen diffusion. Therefore, during deposition and the annealing processes, excess oxygen can easily diffuse through the HfO_2 or ZrO_2 films into the interface area and oxidize the Si substrate.

Similar to SiO_2 alloying with HfO_2 or ZrO_2, adding Al_2O_3 to HfO_2 or ZrO_2 films can also help to stabilize them in an amorphous structure during high temperature annealing.[7,8] However, compared to SiO_2, Al_2O_3 possesses larger relative permittivity and thus will reduce the overall dielectric constant less when alloyed with HfO_2 or ZrO_2. In addition, Al_2O_3 has its own unique advantages such as a large band gap (about 8.8 eV) and large band offset with Si, and Al_2O_3 is also a good barrier to oxygen diffusion and protects the Si surface from oxidation.[3,13] In order to maximize the advantages offered by HfO_2 and Al_2O_3, it is desirable to make a Hf–Al–O film as a high-*k* gate dielectric. Recent reports on aluminates of Zr (Zr–Al–O) (Refs. 7 and 8) and of Hf (Hf–Al–O) (Refs. 14–17) showed that these material systems exhibit encouraging gate dielectric properties. Cho and co-workers reported thermal stability of Al_2O_3/HfO_2 nanolaminates structure on Si.[18] Our preliminary result on the synthesis and characterization of Hf–Al–O films has also shown very encouraging results with excellent thermal stability and electrical performance.[19] In this letter, we focus on the study of interfacial reaction at the Hf–Al–O/Si interface under an oxygen-deficient condition and its impact on dielectric performance.

Hf–Al–O thin films on *p*-type (100) Si substrates were deposited by pulsed-laser deposition (PLD) using a HfO_2 and Al_2O_3 composite target with base vacuum of 5×10^{-5} Pa. In order to avoid the formation of a SiO_2 interfacial layer, the films were deposited at relatively low substrate temperatures (550–700 °C) in a high vacuum environment without introducing any oxygen gas. Si substrates were treated by a conventional HF-last process just before film deposition, leaving a hydrogen termined surface. A KrF excimer laser ($\lambda=248$ nm) with laser fluence of 6 J/cm^2 and repetition rate of 2 Hz was used. Structural characterization was carried out by transmission electron microscopy (TEM) using a JEOL 2010 electron microscope equipped with energy dispersive x-ray (EDX) analysis. Electric properties of the MOS capacitors with Pt dot electrodes were studied by capacitance–voltage (C–V) measurements using a HP4194A impedance analyzer.

Figure 1 shows TEM images of a 60 Å-thick Hf–Al–O thin film grown on a Si substrate at 550 °C. It can be seen

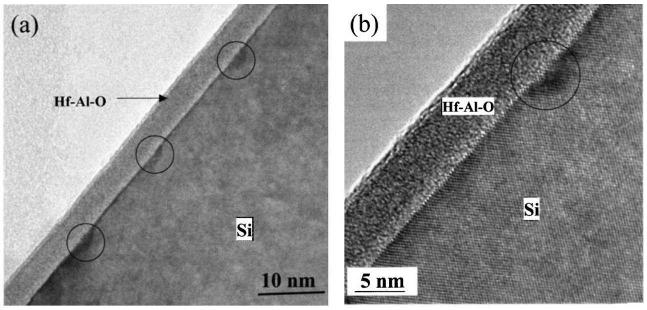

FIG. 1. Cross-sectional TEM images of a thin Hf–Al–O film on a (100) Si substrate. (a) Low magnification and (b) high resolution. The circles indicate the interfacial reaction.

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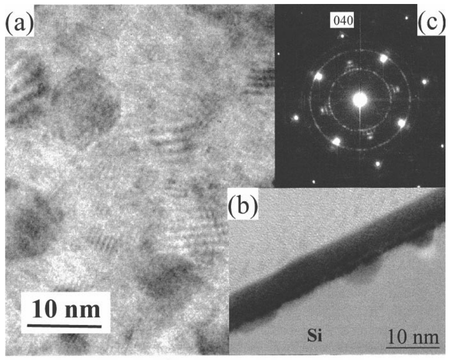

FIG. 2. (a) Low magnification cross-sectional TEM image of a thin Hf–Al–O film on a Si substrate. (b) Cross-sectional TEM image of the same Hf–Al–O film on Si showing interfacial reaction at the interface. (c) Corresponding selected area electron diffraction pattern from the plan-view sample.

that the Hf–Al–O film is a uniform amorphous structure that possesses an atomically flat surface and an interface with Si. In fact, atomic force microscope analysis of the surface morphology revealed a root mean square (rms) roughness of only 2.5 Å. It can also be seen from the low magnification image in Fig. 1(a) that there are some island-shaped precipitates on the Si surface that have darker contrast, suggesting interfacial reaction or diffusion at the interface. These interfacial reactions are generally observed in all samples with different thicknesses deposited over a wide range of temperatures from 550 to 700 °C without introducing any oxygen gas, and it was found that the degree of reaction increases with the growth temperature. The atomic ratio of Al/Hf in the films is about 1.4 as revealed by microbeam EDX analysis. Nanobeam EDX analysis also proved that the island-shaped interfacial reaction producted is Hf silicide. This agrees with the fact that Al usually does not form a silicide bond with Si.

Figure 2(a) is a plan-view TEM image of another Hf–Al–O film grown at 700 °C. Since plan-view TEM observation of amorphous film on Si should show uniform contrast, the grain-like features that appear in Fig. 2(a) indicate a very serious interfacial reaction. It can also be seen that some Hf silicide islands have faceted into hexagons. The moiré fringes that can be identified from the plan-view TEM image are due to overlapping of the silicide islands with the Si substrate that was not milled off by the ion beam. Figure 2(b) is a cross-sectional TEM image of the same film on Si showing the interfacial reaction. The corresponding selected area electron diffraction pattern from the plan-view sample is shown in Fig. 2(c), where the strong diffraction points are from the Si [100] zone axis and the rings and weak points are from Hf silicide. Since the diffraction from Hf silicide contains rings and isolated dots, the silicide formed may contain more than one phase. Phase identification of Hf silicide that formed at the interface will be reported elsewhere.

It is well known that the interfaces of HfO_2/Si and Al_2O_3/Si are thermodynamically stable. However, the formation of Hf silicide at the interface suggests that the interface of Hf–Al–O/Si is not stable. So we have carried out a comparison by depositing Al_2O_3 and HfO_2 films at the same conditions as those for growth of the Hf–Al–O films. The results showed that the interfaces of Al_2O_3/Si and HfO_2/Si were free of silicidation reaction. An interesting question that arises from this is, why are HfO_2/Si and Al_2O_3/Si interfaces stable (free of silicidation) but Hf–Al–O/Si interface is not? There are two possible approaches for answering this question. First, we believe that there is competition between Hf and Al atoms in bonding with limited oxygen atoms when they arrive on the Si surface. Since Al has a very strong affinity to oxygen atoms, for some of the Hf atoms at the Si surface it will be difficult to form an oxide bond. The lack of oxygen for Hf atoms at the interface area is believed to be the reason for Hf silicide formation. It was reported earlier that oxygen-deficient Zr can react with SiO gas phase and form $ZrSi_2$ under high temperature annealing in ultrahigh vacuum conditions.[11,12] There may be a similar mechanism to describe the Hf–Al–O/Si system.

The other approach is related to another question. It is well known that both amorphous and crystalline HfO_2 are thermodynamically stable when in contact with Si. The question is whether the interface is still stable if HfO_2 is in an amorphous structure at temperatures much higher than its transition temperature from amorphous phase to crystalline phase. The answer is uncertain since the Gibbs free energies for HfO_2 in amorphous and crystalline phases at the same temperature are different, and thus the tendency for chemical reaction based on Gibbs energy analysis may change. Our experimental result suggested that if HfO_2 is not in a crystalline structure at high temperatures due to alloying with Al_2O_3, the HfO_2/Si interface may not be thermodynamically stable, especially for oxygen-deficient conditions. A detailed thermodynamic analysis in this Hf–Al–O/Si system is not possible at present due to the lack of enough thermodynamic information.

This Hf silicide reaction is not usually seen in other deposition techniques such as jet-vapor-deposition,[14] atomic layer deposition[15–17] and chemical vapor deposition,[20] where the oxygen (or water vapor) and high temperature are involved during deposition. A sufficient oxygen source and high temperature result in significant SiO_2 interfacial layer formation and thus the silicidation is suppressed. However, Hf aluminate can be grown by PLD without introducing oxygen gas during deposition and oxygen vacancies in the films can be filled by subsequent annealing in oxygen ambient. Therefore, lack of oxygen in the PLD process may result in silicidation. In fact, when oxygen gas was introduced during the PLD process in our experiment, a silicidation-free interface was obtained. By optimizing the oxygen pressure ($\sim 10^{-4}$ Pa), the SiO_2 interfacial layer can be controlled to within 10 Å, and silicidation is inhibited.

Figure 3 shows a high frequency $C-V$ measurement of a thin Hf–Al–O film (60 Å) parallel plate capacitor that contains silicide at the interface. Compared to the well-behaved $C-V$ curve of the sample without silicidation at the interface grown at an optimized oxygen partial pressure (inset in Fig. 3), there is no saturation in the accumulation region but a small hump near $V_{bias} = -1.0$ V is present. These features suggest the presence of a large number of interface traps in the Si band gap.[21] Since the very thin Hf–Al–O film resulted in large leakage current, the $C-V$ measurement at different frequencies showed a large discrepancy. Therefore, only the 1 MHz result is shown in Fig. 3.

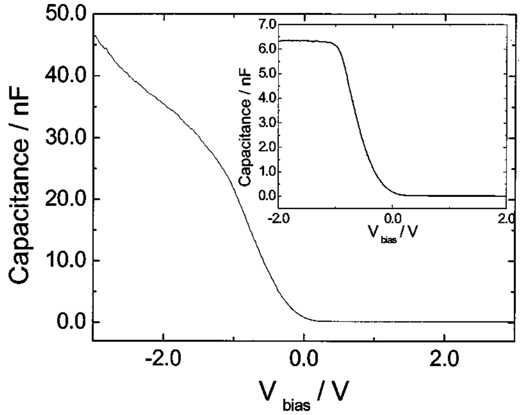

FIG. 3. High frequency (1 MHz) $C-V$ curve of a thin Hf–Al–O film with silicide reaction at the interface. The inset shows a well-behaved $C-V$ curve of a sample without interfacial reaction.

Figure 4 is a characteristic $C-V$ curve of a thicker (300 Å) Hf–Al–O film grown at 700 °C that contains silicide islands at the interface. The driving frequencies are from 100 kHz to 2 MHz. Besides nonsaturation of the accumulation capacitance, similar to that in the thinner film sample, there is another significant feature that needs to be noted in this abnormal $C-V$ curve. A step near the boundary of depletion and weak inversion can be seen (indicated by the arrow), and from that point on the capacitance shows a continuous decrease versus the gate bias voltage. These characteristics are believed to be related to the presence of interfacial silicidation. A silicide island at the Si surface can be considered to be a large density of interfacial traps, and thus is responsible for the large stretching out along the voltage axis of the high frequency $C-V$ curve at depletion and weak inversion.[22] In strong inversion where interfacial traps are not important, we may consider the silicide island to be an extra discontinuous metal layer in between the gate dielectric and the Si substrate.

Under positive gate bias, the metal layer is negatively charged, since minority charge carrier electrons in the inversion areas near the silicide island can drift across the interface of silicide/Si due to attraction of the electric field from the gate. The negatively charged thin metal layer screens the field of high frequency ac signal from the gate and causes the Si depletion capacitance under the silicide island to decrease and thus decreases the overall capacitance. Since the density of negative charges injected from Si into the silicide island increases with the gate bias, the screening effect for the high-frequency ac electric field will increase. Therefore, the overall capacitance decreases as the gate bias increases.

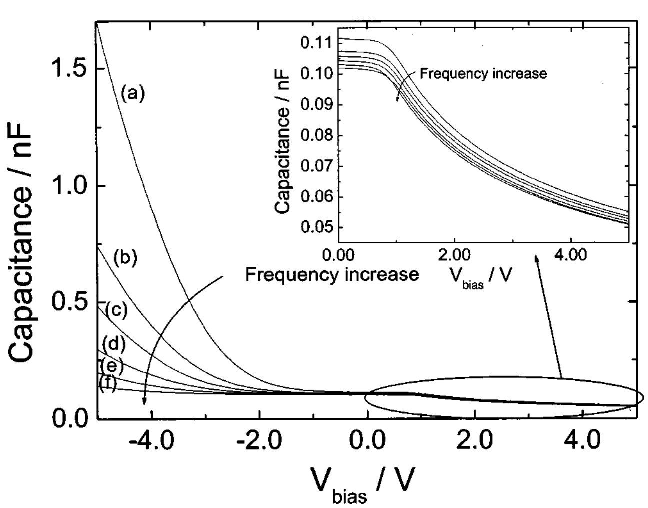

FIG. 4. Characteristic $C-V$ curve of a thicker Hf–Al–O film with interface silicidation. The frequencies are (a) 100 kHz, (b) 200 kHz, (c) 300 kHz, (d) 500 kHz, (e) 1 MHz, and (f) 2 MHz.

In summary, amorphous thin films of Hf–Al–O were deposited on p-type (100) Si substrates by pulsed-laser deposition. TEM analysis revealed Hf silicidation reaction at the Hf–Al–O/Si interface. The Al oxide present in the films retards the formation of crystalline HfO_2, and thus triggers a reaction between the Hf atoms in the amorphous Hf–Al–O film and Si at the oxygen-deficient condition. High-frequency $C-V$ measurements revealed the impact of silicide formation at the interface on the electrical properties, and this impact seems to be both frequency and dielectric thickness dependent.

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