Growth and characterization of Hf–aluminate high-*k* gate dielectric ultrathin films with equivalent oxide thickness less than 10 Å

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Ultrathin amorphous Hf–aluminate (Hf–Al–O) films have been deposited on *p*-type (100) Si substrates by pulsed-laser deposition using a composite target containing HfO_2 and Al_2O_3 plates. Transmission electron microscopy observation of Hf–Al–O films showed that the amorphous structure of Hf–Al–O films was stable under rapid thermal annealing at temperatures up to at least 1000 °C. Capacitance–voltage measurement of a 38 Å Hf–Al–O film revealed that the relative permittivity of the film was about 16. Such a film showed very low leakage current density of 4.6×10^{-3} A/cm^2 at 1 V gate bias. The Hf–Al–O film under optimized condition did not show any significant interfacial layer at the interface and an equivalent oxide thickness of less than 10 Å has been achieved. The formation of Hf–O and Al–O bonds in the film was revealed by x-ray photoelectron spectroscopy. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1554764]

A gate dielectric with a relative permittivity higher than that of SiO_2 is required to meet the next generation complementary metal-oxide-semiconductor (MOS) technology requirement.[1–3] Recent publications show that HfO_2 and ZrO_2 as well as their silicates are becoming leading candidates for high-*k* gate dielectric application due to their thermodynamic stability in contact with Si.[4–9] However, due to the weakness as an oxygen diffusion barrier of HfO_2 and ZrO_2, formation of interfacial SiO_2 rich layer in contact with Si substrate or polysilicon gate material is still a problem affecting the application. Formation of silicide at the interface without oxygen is another serious problem.

Al_2O_3 is a well-known good oxygen diffusion barrier that may protect the Si surface from oxidation,[10,11] and Al_2O_3 is thermodynamically stable in contact with Si. Similar to SiO_2, Al_2O_3 is also a good glass former; thus, if alloyed with ZrO_2 and HfO_2, their amorphous structure can be stabilized during high temperature annealing.[12,13] In addition, Al_2O_3 has a large band gap (8.8 eV) and large band offset with Si. To take advantage of both HfO_2 and Al_2O_3, it is desirable to make multicomponent MAl_xO_y (M=Hf, Zr) films with high dielectric constant that are thermodynamically stable in contact with Si. Recent results on aluminates of Zr (Zr–Al–O) indicate that such material system exhibits encouraging gate dielectric properties.[12,13] Van Dover and co-workers have reported $Zr_{0.62}Al_{0.38}O_{1.8}$ thin film in which the crystallinity starts to appear at 850 °C.[14] Accommodation of Al_2O_3 layer with HfO_2 films in order to increase the interfacial stability with Si has been reported recently,[8,9] and some thermal stability studies on Hf–Al–O films have also been reported recently.[15] Electrical properties such as electron trapping and band alignment in amorphous Hf–Al–O have also been reported.[16,17] However, the understanding of thermodynamic stability and interfacial structure of the Hf–Al–O thin film is still limited. In this article we report the synthesis and characterization of ultrathin Hf–Al–O films for high-*k* gate dielectric application with equivalent oxide thickness less than 10 Å.

The Hf–Al–O ultrathin films on *p*-type (100) Si substrate were deposited by pulse-laser deposition (PLD) using a specially designed target containing HfO_2 and Al_2O_3 plates. The laser frequency was set to 2 Hz and the target rotation was set to a speed in which HfO_2 and Al_2O_3 target was sequentially ablated only one pulse a time during laser ablation. Based on the experimental data, the HfO_2 and Al_2O_3 films' growth rate for each pulse is about 0.2 Å which is much smaller than one single atomic layer. Therefore, the composite films grown by this method can be considered as sublayer laminates of HfO_2–Al_2O_3, and we can expect that such films are comparable with the films made using a target containing HfO_2 and Al_2O_3 particles. The base vacuum of the chamber is 5×10^{-5} Pa, and, in order to reduce the formation of interfacial SiO_2 layer, the films were deposited at a relatively lower substrate temperature 550 °C. Si substrates were treated by a conventional HF-last process before film deposition leaving the hydrogen terminal surface. A KrF excimer laser ($\lambda=248$ nm) with laser fluence of 6 J/cm^{-2} is used for the film deposition. In order to study its structure stability under high temperature, the as-grown films were rapid thermal annealed (RTA) at 1000 °C for 10 s at a vacuum of 10^{-3} Torr. RTA under reduced oxygen pressure (5 Pa) was also performed at 500 °C for 1 min in order to compensate the oxygen loss during film deposition. The structure of the films and the interface with Si substrates before and after annealing was characterized by means of high-resolution transmission electron microscope (TEM) using JEOL 2010 electron microscope equipped with energy dispersive x-ray (EDX) analysis. The chemical structure of the film was characterized using a Physical Electronics Quantum 2000 x-ray photoelectron spectrometer with a monochromatic Al $K\alpha$ (1486.7 eV) source. The scans were done at

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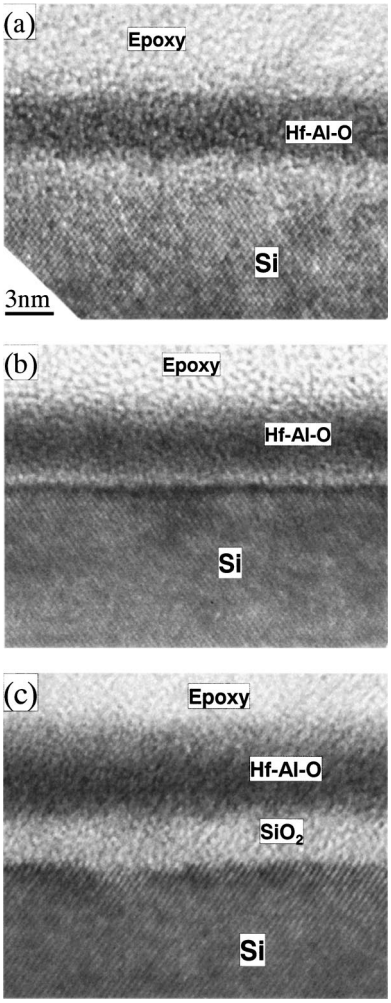

FIG. 1. Cross-section TEM images of thin Hf–Al–O films on *p*-type (100) Si substrates with different annealing conditions. (a) As-grown film, (b) annealed at 500 °C for 1 min with oxygen partial pressure of 5 Pa, and (c) RTA at 1000 °C for 10 s.

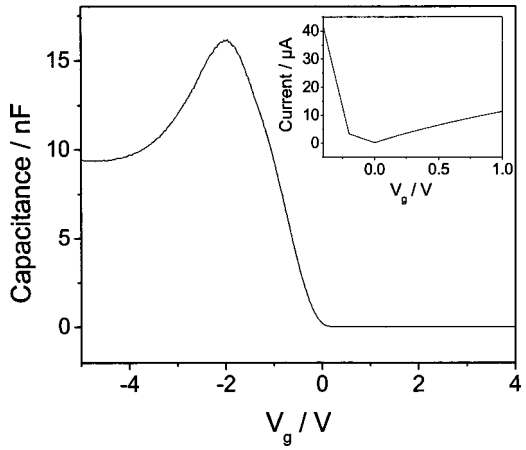

FIG. 2. Characteristic high frequency (1 MHz) *C–V* curve of the parallel plate capacitor with Pt dot electrode on annealed Hf–Al–O film. The inset shows a typical current density–voltage curve.

pass energy of 23.5 eV and a takeoff angle of 90°. All of the spectra are calibrated against C 1*s* peak (284.5 eV) of adventitious carbon and plotted with normalized intensities. Electrical properties of the MOS capacitors with Pt dot electrodes were studied by *C–V* measurements using a HP4194A impedance analyzer. Leakage current of the capacitors was characterized by means of Advantest TR8652 Digital Electrometer. The electrode area was 2.5×10^{-3} cm^2 for both *C–V* and *I–V* measurement.

EDX analysis of the as-grown Hf–Al–O films shows that films generally have a composition of $Hf_{0.14}Al_{0.25}O_{0.61}$. TEM examinations of different temperature annealed Hf–Al–O films revealed that the amorphous structure of the films is stable under all the annealing temperatures up to at least 1000 °C. Figure 1 shows TEM pictures of an ultrathin (about 38 Å) Hf–Al–O amorphous film grown on Si substrate before and after thermal annealing. In Fig. 1(a), the very thin white contrast interfacial layer in the as-grown sample indicates a possible SiO_2 rich layer formed during film deposition. After annealing at 500 °C for 1 min in oxy-

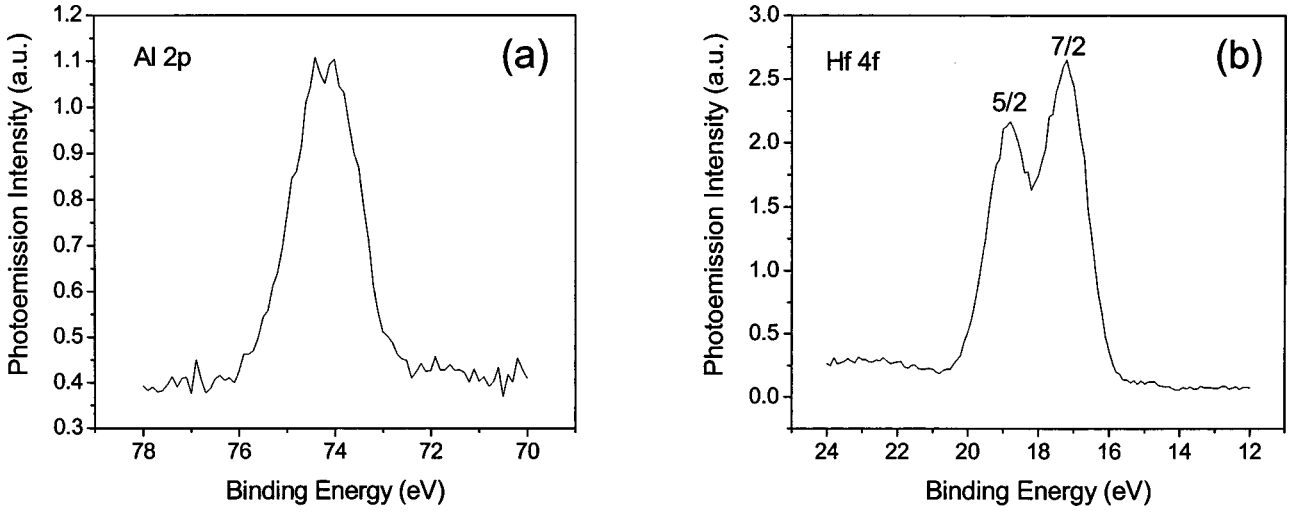

FIG. 3. XPS spectrums of annealed Hf–Al–O ultrathin film on Si substrate. (a) Al 2*p* spectra, and (b) Hf 4*f* spectra. The Hf 4*f* (7/2) peak is 17.2 eV, separated by the 1.7 eV spin splitting from the Hf 4*f* (5/2) peak at 18.8 eV.

gen ambient, there is no further oxidation of the Si substrate as shown in Fig. 1(b). This indicates that the film has sufficientresistance to oxygen diffusion at this condition. It should be pointed out that the interface between Hf–Al–O film and epoxy is not sharp since both of them are amorphous structures. The Hf–Al–O film surface is very flat, in fact, as proved by atomic force microscope analysis that shows only 2 Å of rms roughness.

No evidence of crystallization can be found within all the observed areas in the Hf–Al–O film after RTA performed at 1000 °C for 10 s. Figure 1(c) is a representative high-resolution TEM picture showing amorphous structure of the Hf–Al–O film after 1000 °C RTA. The interfacial layer formed as shown in Fig. 1(c) is a SiO_2 layer due to further oxidation of Si during RTA since the vacuum is not high enough for very high temperature annealing. The very recent report shows that the structural transition from amorphous to crystalline for the Al_2O_3–HfO_2 nanolaminates occurs at a temperature of 920 °C and the laminate is drastically broken.[9] Therefore, the amorphous Hf–Al–O films under our deposition condition show much better thermodynamic stability compared to laminated structure. In fact, a comparison experiment has been carried out to illustrate the high resistance to oxygen diffusion of Hf–Al–O film using HfO_2 film as a control sample. The result (not shown here) revealed that the amorphous Hf–Al–O thin film has much better property to block the oxygen diffusion.

Figure 2 is a characteristic high frequency C–V curve of the 38 Å Hf–Al–O film with bias voltage from −6 to 4 V. The accumulation capacitance is 9 nF, and the peak near the transition on the accumulation side may be caused by too much series resistance.[18,19] The relative permittivity of the Hf–Al–O film is calculated to be about 16 and the equivalent oxide thickness to SiO_2 is 9.2 Å for the sample annealed at 500 °C for 1 min in oxygen ambient. The inset in Fig. 2 is a typical current density–voltage curve of the MOS capacitor, and one can see that at 1 V gate bias voltage, the leakage current density is 4.6×10^{-3} A/cm^2, which is five orders of magnitude higher than that of 10 Å SiO_2.[3]

Formation of Hf–O and Al–O bonds is studied by x-ray photoelectron spectroscopy (XPS) analysis as shown in Fig. 3. Figure 3(a) shows the Al $2p$ peak at 74.2 eV indicating Al_2O_3 formation in the film. The Hf $4f$ peak is shown in Fig. 3(b). It is worth noting that, compared to the reported Hf $4f$ peaks (16.8 and 18.5 eV) for HfO_2,[20] there is a 0.4 eV shift of Hf $4f$ peaks toward higher binding energy for the Hf–Al–O film in our case. Yu *et al.* stated that all the core level peak positions of Hf $4f$, Al $2p$, and O $1s$, experience a shift to higher binding energy with the increase of Al_2O_3 concentration in the Hf–Al–O system.[17] This shift may be attributed to the fact than Hf is a more ionic cation than Al in the Hf–Al–O system, and thus the charge transfer contribution changes with the increase of Al concentration.[17,21,22]

In summary, ultrathin amorphous Hf–Al–O films have been deposited on p-type (100) Si substrates by PLD. TEM examinations of different temperature annealed Hf–Al–O films revealed that the amorphous structure of the film is stable up to at least 1000 °C annealing. Relative permittivity of 16 and an EOT of 9.2 Å have been achieved by a 38 Å amorphous Hf–Al–O film and the film presents very low leakage current of 4.6×10^{-3} A/cm^2. XPS analysis of the Hf–Al–O film shows the formation of Hf–aluminate in the film.

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