Selective atomic layer deposition of HfO_2 on copper patterned silicon substrates

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Selective atomic layer deposition (ALD) was performed on copper patterned silicon substrates to selectively deposit HfO_2 film on silicon. The selectivity is based on differences of surface physics/chemistry rather than use of any molecular masking such as self-assembled monolayers. On silicon, the growth rate of HfO_2 is 0.11 nm /cycle with no initial inhibition of film growth, while on copper no HfO_2 deposition was observed up to at least 25 ALD cycles. The selective growth on silicon over copper at 25 ALD cycles provides a patterned film deposition at thicknesses of 2.8 nm HfO_2 which is relevant to semiconductor nanofabrication. © *2010 American Institute of Physics*.
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Atomic layer deposition (ALD) is a powerful means of fabricating nanoscale features in three-dimensional structures which have importance in a wide range of applications such as solid oxide fuel cells,[1,2] memory storage,[3,4] and chemical sensors.[5] In the fabrication of semiconductor devices, ALD has been used extensively to create gate oxide layers in field effect transistors, dielectric layers in capacitive memory cells, and diffusion barrier layers for copper interconnects of semiconductor logic processing units. In all these applications, patterning of the ALD film is required for device functionality. The patterning can be done subtractively by global deposition followed by selective removal of the film or by selective atomic layer deposition (SALD).

SALD is a more efficient process in that it eliminates the selective removal steps often involving combinations of chemical etch with expensive reagents and photolithography. For this reason, there is a lot of interest in selective deposition techniques. The most common approach of SALD is to provide a molecular mask over selected nondeposited areas. In recent years several self assembled monolayer materials have been effective in preventing deposition;[6] specifically for the ALD of HfO_2, several self-assembled monolayers (SAMs) have been evaluated.[7] However, SAMs typically have long assembly times of the order of hours before impervious layer is established to fully prevent deposition and require removal after deposition. An alternate and more efficient approach to SALD is to take advantage of the different materials at the surface having different nucleation times for film growth by ALD. For example, the ALD of HfO_2 on bare silicon exhibits an inhibited growth due to lack of hydroxyl surface sites for ALD; however, in this case the nucleation time is quite short and on the order of only a couple of ALD cycles.[8] Nonetheless, surprisingly this surface dependence for different materials has not been evaluated at length despite the useful benefit especially as deposited layers approach a few nanometers thickness.

In these experiments, about 2×2 cm^2 sections of silicon (100) substrates were partially coated with copper using electron beam evaporation (Varian model no. NRC3117). The electron beam was provided with a 10 kV voltage having 175 mA current resulting in 0.24 nm/sec copper deposition. In this manner, ~200 nm thick copper coating was deposited on the patterned substrates over a portion of the silicon substrate whereas the other portion (about one-half of the silicon substrate) was masked during the evaporation process in order to prepare the partially copper coated silicon substrates. Both copper and silicon portions of the substrates have oxide on the surface and the thicknesses of these oxides were measured using a spectral ellipsometer (Woollam M-44). Immediately after evaporation, the surface oxide on copper was about 0.5 nm with no noticeable change over a few hours interval, and 1.5 nm native oxide on silicon. To minimize any additional oxidation of the copper surface, the ALD of HfO_2 was done within one hour after copper partially coated the silicon substrate. After ALD, samples were analyzed by spectral ellipsometry and x-ray photoelectron spectroscopy (XPS, Kratos AXIS-165) equipped with a monochromatic Al $K\alpha$ (1486.6 eV) x-ray source and concentric hemispherical analyzer coupled with a charge neutralizer operated at 15 kV and 10 mA.

The ALD of hafnium oxide made use of tetrakis (diethylamino) hafnium (TDEAH) with water vapor as the oxidizer within a hot wall ALD reactor maintained at 200 °C. Further details of the ALD reactor can be found elsewhere.[9,10] In these studies, 0–50 ALD cycles were used on the copper patterned silicon substrates in order to probe and evaluate selectivity of ALD on both silicon and copper surfaces simultaneously on the same substrate. The ALD kinetics of HfO_2 under these conditions on silicon has been previously examined[11] and under these typical reactor conditions, a self-limited ALD rate of 0.11 nm/cycle is observed with excellent linearity with respect to the number of applied ALD cycles, without an initial inhibition period.

Figure 1 shows XPS survey scans of copper and silicon portions of the substrate after 0, 25, and 50 ALD cycles of HfO_2 on three copper patterned silicon substrates. The spectra labeled (a) through (c) represent survey scans on the silicon portion of the substrates, while spectra labeled (d)

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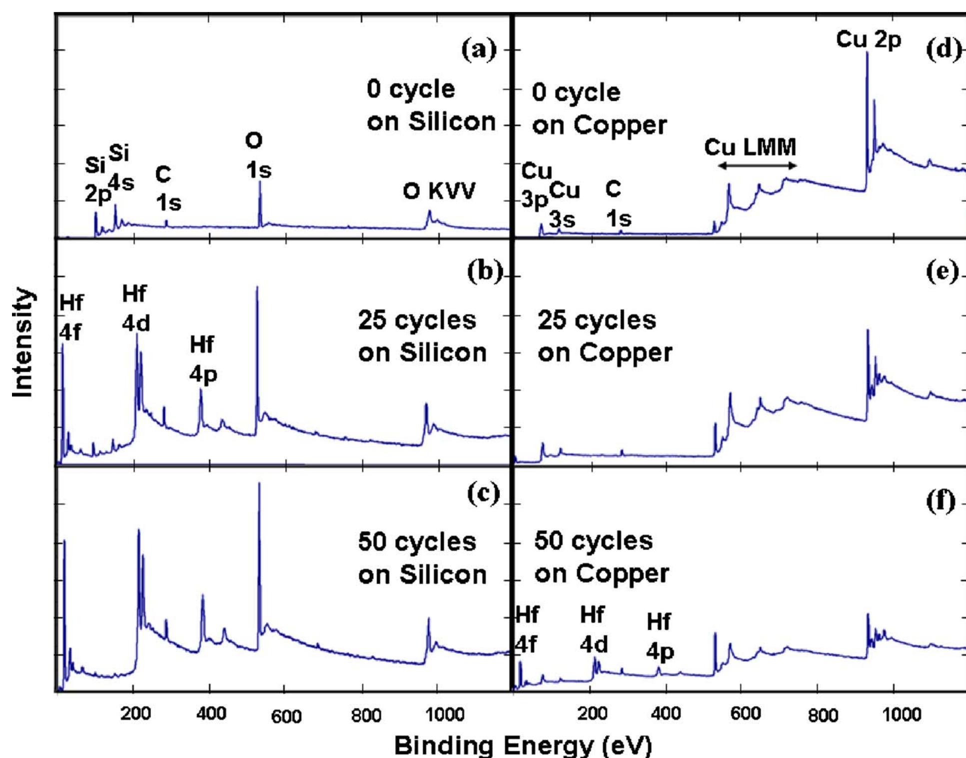

FIG. 1. (Color online) 0, 25, and 50 ALD cycles of HfO_2 on Si [(a)–(c)] and Cu [(d)–(f)]; (a) and (d) corresponds to 0 cycle, (b) and (e) to 25 cycles, and (c) and (f) to 50 cycles. ALD reaction temperature is 200 °C and the pressure is 0.18 Torr.

through (f) represent survey scans on the copper portion of the substrates. Prior to deposition, XPS analysis of the silicon surface indicates only Si, O, and C elements [Fig. 1(a)]. The carbon is the result of surface contamination[11] and the oxygen comes from the native oxide on the silicon surface. After 25 and 50 ALD cycles [Figs. 1(b) and 1(c), respectively], several XPS peaks appeared on the silicon portion of the substrate which correspond to Hf 4*f* (15.5–20.3 eV), Hf 4*d* (213.7–225.8 eV), and Hf 4*p* (382.5 and 440.3 eV). The intensity of these XPS peaks increases with increasing number of ALD cycles, while at the same time, the Si 2*p* (98.0 eV) and 4*s* (150.1 eV) peak intensities decrease due to the growth of HfO_2 on top of the silicon surface. The thicknesses of the resulting HfO_2 films on silicon after 25 and 50 cycles are 2.8 nm and 5.4 nm, respectively, as measured by ellipsometry and they are consistent with our previously evaluated HfO_2 ALD rate of 0.11 nm/cycle on patternless silicon substrates.

On the copper portion of the substrate with no ALD cycles, the XPS survey scan shows Cu 2*p* (932.2 and 952.0 eV) which indicates that copper is mainly in the metallic state [Fig. 1(d)].[12] A small O 1*s* peak is also observed which is consistent with the trace presence of native copper oxide on the surface which was also detected by ellipsometry. After 25 ALD cycles of HfO_2, the XPS analysis still shows no hafnium-containing species on the copper portion of the substrate [Fig. 1(e)]. Compared to Hf 4*f* peak of HfO_2 on silicon at 25 cycles, this result represents at least a 50-fold reduction in Hf on the copper surface at 25 cycles indicating less than one monolayer of Hf on the copper surface. The XPS peaks observed beyond 570 eV binding energies correspond to copper with trace amounts of surface oxide as noted in Figs. 1(d)–1(f) with slight increase in oxides after ALD due to air oxidation of the copper upon removal from the heated reactor while still hot.

After a further increase in the HfO_2 ALD cycles to 50 [Fig. 1(f)], Hf 4*f* and Hf 4*d* peaks become detectable indicating eventual HfO_2 growth on the copper surface. The significant time delay in the formation of HfO_2 on copper indicates the need for surface site nucleation of HfO_2 on copper which is not present on silicon. This is surprising since both copper and silicon have native oxides on the surface. It is noted that in Fig. 1(f) the intensity of the Cu 2*p* peaks decreased after 50 ALD cycles, further supporting the deposition on copper after that number of cycles.

Elemental compositions shown in Table I are calculated from quantitative analysis of the XPS spectra of the corresponding elements. The increased amounts of hafnium and oxygen along with the decreased amounts of silicon from 0 to 50 ALD cycles indicate the continuous growth of HfO_2 films on the silicon portion of the substrates. On the other hand, HfO_2 deposition on the copper portion of surfaces is observed only when more than 25 ALD cycles of TDEAH/H_2O are used.

Figure 2 shows XPS core spectra of Hf 4*f* after 25 and 50 ALD cycles of HfO_2 on both silicon and copper portions of the substrate surface. All spectra except the 25 ALD cycles of hafnium oxide on copper show the typical Hf peaks at 17.0 eV, Hf $4f_{7/2}$ and at 18.6 eV, Hf $4f_{5/2}$. No shoulder peak at lower binding energy is observed indicating no formation of other hafnium species, such as hafnium silicide,

TABLE I. Elemental compositions (at. %) on Si and Cu parts of substrate surfaces determined by XPS after 0, 25, and 50 cycles of ALD hafnium oxide.

On silicon (elemental composition, at. %)				On copper (elemental composition, at. %)		
Hf	Si	O	ALD cycles	Hf	Cu	O
0	58	42	0	0	76	24
24	18	58	25	0	53	47
32	3	65	50	13	25	62

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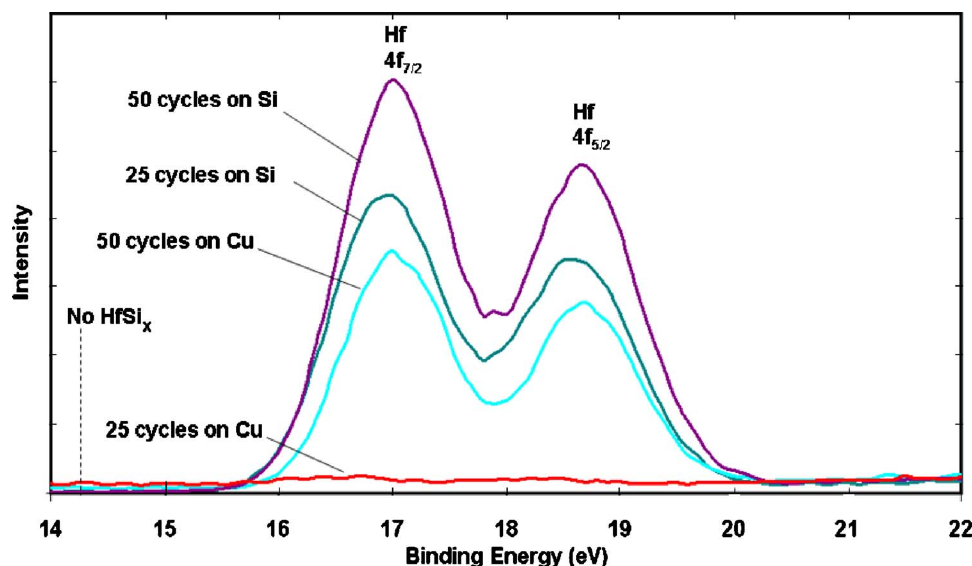

FIG. 2. (Color online) XPS core scans after 25 and 50 ALD cycles of HfO_2 ALD on silicon and copper surfaces of patterned substrates. Experimental conditions for these samples are the same as those in Fig. 1.

during the deposition.[13,14] From the Hf 4f core data after 25 ALD cycles on silicon and copper portions, the selective growth of HfO_2 on silicon over copper, that is, without any detectable HfO_2 growth on the copper surface, is again demonstrated and clearly evident; at the same time, 2.8 nm of HfO_2 forms on the silicon surface. When the number of the ALD cycles increased to 50, it is found that there is a small amount of HfO_2 on the copper surface of the substrate indicating considerable delay in the formation of HfO_2 on copper surfaces and a significantly smaller amount of HfO_2 formed on copper than that on silicon. The likely explanation of this selectivity of HfO_2 ALD on silicon over copper is a significantly longer nucleation time for the HfO_2 ALD on copper than that on silicon, as silicon oxide easily accommodates hydroxyl sites at the surface. As a result, a growth inhibition period of HfO_2 on the copper surface is observed at a number of ALD cycles greater than 25. Further studies are needed to examine in detail the factors leading to surface selectivity and potentially identify means of further extending the inhibited growth on metallic copper and other surfaces relevant to nanofabrication of patterned thin film deposition used today.

In conclusion, copper patterned silicon substrates with different number of ALD cycles of HfO_2 have been carried out with films characterized by spectroscopic ellipsometry and XPS. The growth rate on the silicon portion of the copper patterned silicon substrate is 0.11 nm/cycle, which is similar to that previously observed on patternless silicon. XPS spectra show highly selective ALD growth of HfO_2 on the silicon surface over copper surface up to at least 25 ALD cycles, and this permits HfO_2 selective growth up of ~3 nm on the silicon portion of substrate with less than one monolayer ALD HfO_2 layer on the copper portion of substrate. In the current trends of semiconductor manufacturing, ~3 nm HfO_2 is sufficient in, for example, copper diffusion barrier layer on interlevel dielectrics. Therefore, such selectivity of ALD on different surfaces without any special surface modification can be quite significant and can have major impact on the nanofabrication of semiconductor devices in the future.

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