Selective Atomic Layer Deposition of TiO₂
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ABSTRACT

A selective atomic layer deposition of TiO₂ on Si and SiO₂ in preference to SiCOH has been developed. This process utilizes Ti(OPr)₃ and acetic acid (AcOH) as the co-reactants and deposits TiO₂ on Si and SiO₂ but not on SiCOH. It is found that 3 nm of TiO₂ may be grown on Si and SiO₂ before significant deposition on SiCOH occurs and the deposited films have RMS roughnesses of 2-3 Å. The selectivity is attributed to the inherent non-reactivity of CH₃ groups on SiCOH and the mechanism is shown to proceed via activation of the Si-H, Si-OH, and Ti-O-Pr surfaces by reaction with AcOH.

INTRODUCTION

As lithography is reaching its fundamental scaling limit, selective chemical deposition methods are becoming a requirement for further scaling of transistors using double patterning techniques. Furthermore, water-free ALD is desirable because water can corrode metals at high temperature and damage the low-k dielectric SiCOH. Water-free atomic layer deposition (ALD) of TiO₂ has been studied using Ti(OPr)₃ and TiCl₄; however, to the best of our knowledge, the selectivity of this precursor combination has not been studied. TiO₂ ALD using Ti(OPr)₃ and AcOH has also been studied; however, again the selectivity of this process was not investigated. In this work a water-free TiO₂ ALD using Ti(OPr)₃ and AcOH is reported which is selective for Si and SiO₂ in preference to -CH₃ terminated SiCOH.

RESULTS

The selective ALD of TiO₂ was tested on Si, SiO₂ and SiCOH. Besides being a typical low-k dielectric, SiCOH is a model system for perfectly passivated SiO₂ since SiCOH is terminated in Si-O-C₃H₃ groups and should not contain any -OH groups. The Si, SiO₂ and SiCOH samples were loaded onto the same sample holder and subjected to the ALD together in order to ensure that all three samples received identical ALD conditions. The results of the TiO₂ ALD using Ti(OPr)₃ and AcOH at 250°C on Si, SiO₂ and SiCOH are shown in Figure 1. It is seen in Fig. 1a & 1b that the first 20 ALD cycles nucleated the TiO₂ on Si and SiO₂, and there was roughly the same amount of deposition on Si as on SiO₂. After a total of 240 ALD cycles there was 3-4 nm TiO₂ deposited on Si and ~3 nm TiO₂ deposited on SiCOH.

Figure 2. AFM images of the TiO₂ film on (a) Si, (b) SiO₂ and (c) SiCOH after a total of 240 ALD cycles of Ti(OPr)₃ and AcOH at 250°C. (a) The TiO₂ film on Si has an RMS roughness of 2 Å. The smoothness of this film is consistent with ALD. (b) The TiO₂ film on SiO₂ has an RMS roughness of 3 Å. (c) The RMS roughness of the SiCOH surface after the ALD cycles is 8 Å. Large (~6nm) particles are observed scattered on the SiCOH surface. These particles are too big to have been grown by ALD and therefore may indicate a slight CVD component.

Figure 3. XPS chemical composition of (a) HF cleaned Si and degreased SiCOH, (b) after dosing with AcOH at 250°C, (c) after dosing with Ti(OPr)₃, (d) after dosing with ACOH again and (e) after dosing with Ti(OPr)₃ again. (a) HF cleaned Si has some O and C contamination. (b) Dosing with AcOH at 250°C did little to both substrates. (c) Ti(OPr)₃ nucleation on Si occurs via a slow CVD component at 250°C. (d) No change in chemical composition is seen from dosing AcOH, however a change in the C oxidation state occurs (see Figure 4). (e) After an incubation period of 200 doses Ti(OPr)₃ a second 200 doses of Ti(OPr)₃ increases the Ti% from ~12 to ~28%. This shows that there is TiO₂ ALD in combination with a small Ti(OPr)₃ CVD component.
SiO$_2$. Conversely, it is seen in Fig. 1c that the first and second 20 ALD cycles deposited no Ti on SiCOH. Only after 100 ALD cycles were dosed onto SiCOH, TiO$_2$ nucleated on SiCOH, and after a total of 240 cycles there was only ~0.5 nm TiO$_2$ on SiCOH. This is consistent with Si-CH$_3$ termination prevent reaction with both precursors.

The samples were removed from the chamber and AFM was performed to quantify surface morphologies (Figure 2). In Fig. 2a, it is seen that the TiO$_2$ film deposited on Si had an RMS roughness of 2 Å. The high conformity of this film is consistent with ALD. In Fig. 2b, it is seen that the TiO$_2$ film deposited on SiO$_2$ had an RMS roughness of 3 Å. The high conformity of this film is also consistent with ALD. Conversely, on SiCOH, large (~6nm) particles are observed scattered on the surface (Fig. 2c). The films grown on Si and SiO$_2$ are only 3-4 nm thick and so any ALD nuclei on SiCOH should also be 3-4 nm tall. The particles on SiCOH are too tall to have been grown by ALD and are not dense enough to explain the 11% Ti on SiCOH; therefore the particles on SiCOH may be indicative of a slight CVD component which might be eliminated with better reactor design.

A saturation experiment was performed to document ALD reactions. The chemical composition of Si and SiCOH substrates subjected to saturation doses of AcOH and Ti(OPr)$_4$ at 250°C were determined by XPS. Figure 3a shows the composition of the HF cleaned Si and degreased SiCOH substrates. All of the Si was in an oxidation state of 0 which is consistent with the HF clean having removed all of the Si-O bonds. No assumptions were made about which precursor would nucleate the ALD and so the substrates were dosed first with AcOH (Fig. 3b). Only a decrease in the C on Si was observed which can be attributed to a modest desorption from the samples being heated to 250°C in vacuum. If AcOH had reacted with the Si surface and left behind a surface -OAc group, a higher binding energy component in the C 1s XPS spectrum should have been observed along with increase O; however, these effects were not observed. Next the samples were subjected to doses of Ti(OPr)$_4$ (Fig. 3c). The TiO$_2$ nucleation on Si occurs by a slow CVD-like dissociative chemisorption of Ti(OPr)$_4$, as evidenced by the slow growth and lack of saturation of Ti on the surface. Next the samples were dosed with AcOH (Fig. 3d). While there is no evident change in the chemical composition of the surface, the AcOH induced formation of a high binding energy component in the C 1s XPS spectrum on Si (see Figure 4). This higher binding energy component is attributed to one of the carbons in a surface -OAc group resulting from ligand exchange of a Ti-OPr species with Ti-OAc. Next the samples were dosed again with Ti(OPr)$_4$ at 250°C (Fig. 3e). The first 200 doses of Ti(OPr)$_4$ did not grow any TiO$_2$ on Si. However, the second 200 doses of Ti(OPr)$_4$

grew ~16% Ti on Si. This enhancement of the growth rate after dosing with AcOH shows that the Ti(OPr)$_4$ + AcOH is an ALD process in combination with a small CVD component at 250°C.

Figure 4 shows the XPS C 1s spectra on the TiO$_2$ film grown on Si after alternating doses of Ti(OPr)$_4$ and AcOH at 250°C. It is seen that A nucleating the ALD with a small amount of Ti(OPr)$_4$, all of the C has a binding energy of 284–288 eV (Fig. 4a). This is consistent with surface Ti-OPr ligands. Conversely, after dosing with AcOH, a higher binding energy C component is observed (Fig. 4b). This higher binding energy component is consistent with surface -OAc groups. It is seen that this higher binding energy C component disappears after subsequent dosing with Ti(OPr)$_4$ (Fig. 4c). The data is consistent with the chemical mechanism shown in Figure 5. The growth is nucleated by the slow reaction of Ti(OPr)$_4$ with the Si-H terminated surface. Si-H bonds are more reactive than the -OAc terminated SiCOH surface and so the nucleation is selective for Si over SiCOH. Dosing with AcOH replaces a Ti-OPr group with a Ti-OAc group. This Ti-OAc group is reactive towards subsequent Ti(OPr)$_4$ molecules. The overall mechanism is activation of the Ti-OPr surface by reaction with AcOH.

**Figure 5. Mechanism of the selective ALD of TiO$_2$ using Ti(OPr)$_4$ and AcOH at 250°C.** The mechanism involves the activation of the surface by reaction with AcOH, making it reactive towards Ti(OPr)$_4$ again.

**CONCLUSION**

A selective water-free atomic layer deposition of TiO$_2$ using Ti(OPr)$_4$ and AcOH at 250°C has been developed. This process relies upon the reaction of AcOH with a Ti-OPr terminated surface to give a Ti-OAc terminated surface which is reactive towards subsequent dosing of Ti(OPr)$_4$. The origin of the selectivity is attributed to the inherent non-reactivity of -CH$_3$ terminated surfaces, such as SiCOH and other low k dielectrics. In addition, this selectivity shows that an appropriate small molecule passivant is used on SiO$_2$, selectivity may be attained for deposition on Si in preference to SiO$_2$.

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**REFERENCES**

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