

Selective Atomic Layer Deposition of TiO₂

Christopher Ahles[†], Jong Choi[†], Keith Wong[§], Srinivas Nemani[§] and Andrew Kummel^{†,‡}

[†]Materials Science and Engineering Program and [‡]Department of Chemistry and Biochemistry,
University of California, San Diego, La Jolla, California 92093, United States

[§]Applied Materials, Sunnyvale, California 94085, United States

Email: cahles@ucsd.edu

ABSTRACT

A selective atomic layer deposition of TiO₂ on Si and SiO₂ in preference to SiCOH has been developed. This process utilizes Ti(OⁱPr)₄ 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-OⁱPr 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(OⁱPr)₄ and TiCl₄; however, to the best of our knowledge, the selectivity of this precursor combination has not been studied.^{1,2} TiO₂ ALD using Ti(OⁱPr)₄ and AcOH has also been studied; however, again the selectivity of this process was not investigated.³ In this work a water-free TiO₂ ALD using Ti(OⁱPr)₄ 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-C_xH_y 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(OⁱPr)₄ 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

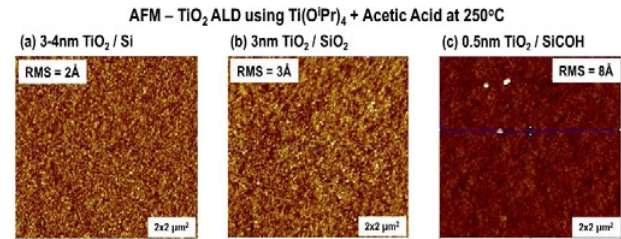


Figure 2. AFM images of the TiO₂ film on (a) Si, (b) SiO₂ and (c) SiCOH after a total of 240 ALD cycles of Ti(OⁱPr)₄ and AcOH at 250°C. (a) The TiO₂ film on Si has an RMS roughness of 2 Å. The smoothness of this film is consistent with ALD. (b) The TiO₂ film on SiO₂ has an RMS roughness of 3 Å. (c) The 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.

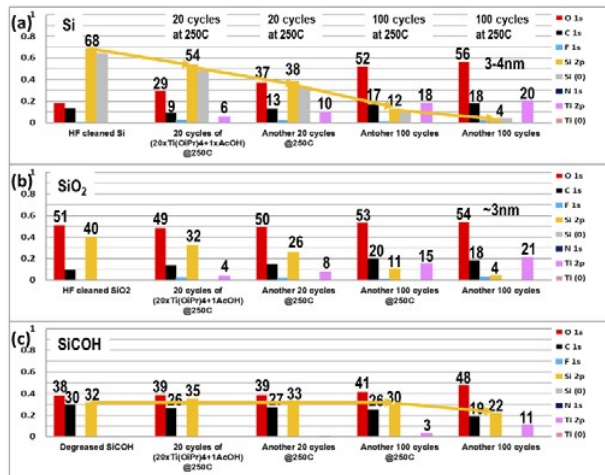


Figure 1. XPS chemical composition of (a) Si, (b) SiO₂ and (c) SiCOH surfaces subjected to TiO₂ ALD cycles using Ti(OⁱPr)₄ and AcOH at 250°C. (a) After a total of 240 ALD cycles there is approximately 3-4 nm of TiO₂ deposited on Si (calculated based on attenuation of the Si substrate signal). (b) After a total of 240 ALD cycles there is approximately 3 nm of TiO₂ deposited on SiO₂ (calculated based on attenuation of the Si substrate signal). (c) After a total of 240 ALD cycles there is 11% Ti on the SiCOH surface. This corresponds to approximately 0.5 nm TiO₂, based on attenuation of the Si substrate signal. The TiO₂ deposition was selective for Si and SiO₂ for the first 140 ALD cycles which deposited ~2 nm TiO₂ on Si and SiO₂ while depositing only 3% Ti on SiCOH (<0.1 nm).

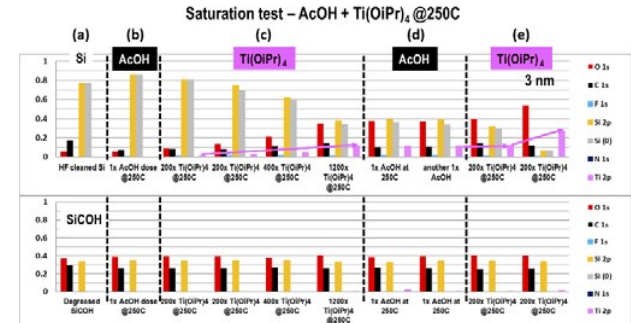


Figure 3. XPS chemical composition of (a) HF cleaned Si and degraded SiCOH, (b) after dosing with AcOH at 250°C, (c) after dosing with Ti(OⁱPr)₄, (d) after dosing with AcOH again and (e) after dosing with Ti(OⁱPr)₄ again. (a) HF cleaned Si has some O and C contamination. (b) Dosing with AcOH at 250°C did little to both substrates. (c) Ti(OⁱPr)₄ 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(OⁱPr)₄ a second 200 doses of Ti(OⁱPr)₄ increases the Ti% from ~12 to ~28%. This shows that there is TiO₂ ALD in combination with a small Ti(OⁱPr)₄ CVD component.

SiO₂. 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, TiO₂ nucleated on SiCOH, and after a total of 240 cycles there was only ~0.5 nm TiO₂ on SiCOH. This is consistent with Si-CH₃ termination preventing 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 TiO₂ film deposited on Si had an RMS roughness of 2 Å. The high conformality of this film is consistent with ALD. In Fig. 2b, it is seen that the TiO₂ film deposited on SiO₂ had an RMS roughness of 3 Å. The high conformality of this film is also consistent with ALD. Conversely, on SiCOH, large (~ 6 nm) particles are observed scattered on the surface (Fig. 2c). The films grown on Si and SiO₂ 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(OⁱPr)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(OⁱPr)₄ (Fig. 3c). The TiO₂ nucleation on Si occurs by a slow CVD-like dissociative chemisorption of Ti(OⁱPr)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-OⁱPr species with Ti-OAc. Next the samples were dosed again with Ti(OⁱPr)₄ at 250°C (Fig. 3e). The first 200 doses of Ti(OⁱPr)₄ did not grow any TiO₂ on Si. However, the second 200 doses of Ti(OⁱPr)₄

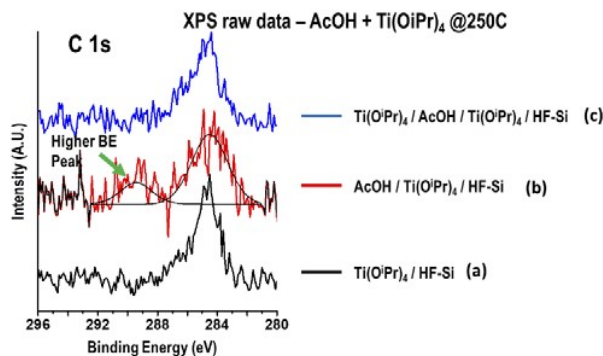


Figure 4. C 1s XPS raw data of a TiO₂ film grown on Si after Ti(OⁱPr)₄ and AcOH half-cycles at 250°C. (a) The C 1s signal after a total of 2,000 doses of Ti(OⁱPr)₄ at 250°C. (b) After dosing with AcOH a higher binding energy component is observed. This is consistent with surface -OAc groups. (c) Dosing with Ti(OⁱPr)₄ again removes this higher binding energy component. This is consistent with ALD via sequential ligand exchange reactions.

grew ~16% Ti on Si. This enhancement of the growth rate after dosing with AcOH shows that the Ti(OⁱPr)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 TiO₂ film grown on Si after alternating doses of Ti(OⁱPr)₄ and AcOH at 250°C. It is seen that after nucleating the ALD with a small amount of Ti(OⁱPr)₄, all of the C has a binding energy of 284-288 eV (Fig. 4a). This is consistent with surface Ti-OⁱPr 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(OⁱPr)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(OⁱPr)₄ with the Si-H terminated surface. Si-H bonds are more reactive than the -CH₃ terminated SiCOH surface and so the nucleation is selective for Si over SiCOH. Dosing with AcOH replaces a Ti-OⁱPr group with a Ti-OAc group. This Ti-OAc group is reactive towards subsequent Ti(OⁱPr)₄ molecules. The overall mechanism is activation of the Ti-OⁱPr surface by reaction with AcOH.

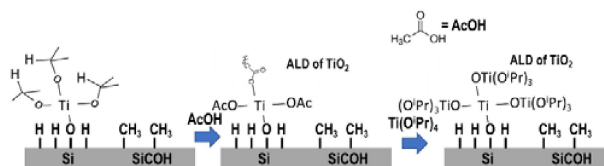


Figure 5. Mechanism of the selective ALD of TiO₂ using Ti(OⁱPr)₄ and AcOH at 250°C. The mechanism involves the activation of the surface by reaction with AcOH, making it reactive towards Ti(OⁱPr)₄ again.

CONCLUSION

A selective water-free atomic layer deposition of TiO₂ using Ti(OⁱPr)₄ and AcOH at 250°C has been developed. This process relies upon the reaction of AcOH with a Ti-OⁱPr terminated surface to give a Ti-OAc terminated surface which is reactive towards subsequent dosing of Ti(OⁱPr)₄. The origin of the selectivity is attributed to the inherent non-reactivity of -CH₃ terminated surfaces, such as SiCOH and other low k dielectrics. In addition, this selectivity shows that if an appropriate small molecule passivant is used on SiO₂, selectivity may be attained for deposition on Si in preference to SiO₂.

ACKNOWLEDGEMENTS

This work was supported by Applied Materials.

REFERENCES

1. V. Anderson et al., JVST A 32, 01A114 (2014).
2. R. Chaukulkar et al., JVST A 31, 031509 (2013).
3. K. Ramos et al., Chem. Mater. 2013, 25, 1706-1712.