In situ ATR-FTIR Study of the Surface Reactions During Atomic Layer Deposition of TiO₂

Li Wang Ye, Theodosia Gougousi
Department of Physics, University of Maryland, Baltimore County

Introduction

Atomic layer deposition (ALD) of high k dielectrics on III-V semiconductors has been shown to have great potentials in high speed metal-oxide-semiconductor field effect transistors (MOSFET). The interface between the high k dielectrics and the substrates is critical to the properties of the devices. Understanding the surface reaction mechanisms during the ALD of high k dielectrics is significant for improving the interfacial properties. In this project, we utilize in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to study the surface reactions during the ALD of TiO₂ on Si (100) and GaAs (100) surfaces from tetraethyl orthoformate (TDMAT) and H₂O.

ALD TiO₂ on Si (100) surfaces

- Si-H modes indicate the formation of H-terminated surface.
- Formation of chemical oxide removes the Si-H bonds and forms hydrophilic surface.

Differential FTIR spectra of the hydrogen terminated (H-Si) and the chemical oxide (CO) Si (100) surfaces.

ALD TiO₂ on chemical oxide (CO) Si (100) at 100°C

- The alternate TDMAT adsorbed and Ti-OH terminated surface indicate the cyclic ALD process.
- Some CH bonds associated with reaction products form and accumulate during the deposition. These are CHs associated with ligand mediated adsorption.

ALD TiO₂ on chemical oxide (CO) Si (100) at 200°C

- Si-H bonds were consumed gradually during the deposition.

ALD TiO₂ on H-Si (100) at 100°C

- During the deposition on both CO and H-Si surfaces, the amount of adsorbed TDMAT increase then decreases and reaches steady state at around 20th cycle.

ALD TiO₂ on H-Si (100) at 200°C

- Si-H bonds are removed by heating.
- Consumed slowly during the deposition.
- About 50% of them still remain after 20 cycles of deposition.

Uptake of TDMAT during the deposition

- The alternate TDMAT adsorbed and Ti-OH terminated surface indicate the cyclic ALD process.
- Some CH bonds associated with reaction products form and accumulate during the deposition. These are CHs associated with ligand mediated adsorption.

Stability of Si-H bonds during the deposition

- Si-H bonds were consumed gradually during the deposition.

ALD TiO₂ on chemical oxide (CO) GaAs at 100°C

- Adsorption of TDMAT on BOE etched GaAs surface is confirmed by the CH and NC₂ vibration modes.
- Formate species form after H₂O dose and accumulate during the deposition.

ALD TiO₂ on chemical oxide (CO) GaAs at 200°C

- Adsorption of TDMAT on BOE etched GaAs surface is confirmed by the CH and NC₂ vibration modes.
- Formate species form after H₂O dose and react with the subsequent TDMAT.
- The accumulation of the formate species during the deposition indicates their incomplete reaction with TDMAT.

Note: The wavenumbers in black indicates the peaks belong to the adsorbed TDMAT; red indicates they do not.

ALD TiO₂ on GaAs (100) surfaces

- The removal of As and Ga oxides by BOE etching is confirmed (F GaAs).
- The growth of As and Ga oxides on F GaAs surfaces in H₂O solution is confirmed (CO GaAs).

ALD TiO₂ on H-Si (100) at 100°C

- The alternate TDMAT adsorbed and Ti-OH terminated surface indicate the cyclic ALD process.
- Some CH bonds associated with reaction products form and accumulate during the deposition. These are CHs associated with ligand mediated adsorption.

Differential FTIR spectra of the CO and F GaAs surfaces.

ALD TiO₂ on H-Si (100) at 200°C

- Si-H bonds were consumed gradually during the deposition.

ALD TiO₂ on chemical oxide (CO) GaAs at 100°C

- Adsorption of TDMAT on BOE etched GaAs surface is confirmed by the CH and NC₂ vibration modes.
- Formate species form after H₂O dose and accumulate during the deposition.

ALD TiO₂ on chemical oxide (CO) GaAs at 200°C

- Adsorption of TDMAT on BOE etched GaAs surface is confirmed by the CH and NC₂ vibration modes.
- Formate species form after H₂O dose and react with the subsequent TDMAT.
- The accumulation of the formate species during the deposition indicates their incomplete reaction with TDMAT.

Note: The reference for the top spectrum is the chemical oxide surface. The other four spectra are differential spectra.

ALD TiO₂ on BO etched (F) GaAs at 100°C

- For the deposition on both CO and F GaAs surfaces, steady state is reached around 20th cycle.

ALD TiO₂ on BO etched (F) GaAs at 200°C

- For the deposition on both CO and F GaAs surfaces, steady state is reached around 20th cycle.

Conclusions

- Cyclic ALD process during the deposition on both chemical oxide and BOE etched Si and GaAs surfaces is confirmed.
- Formate species form and accumulate during the deposition of TiO₂ on both Si and GaAs surfaces.
- Some CH bonds associated with ligand mediated adsorption accumulate during the deposition.

Acknowledgements

- NSF CAREER award (DMR-0846445)
- Materials and Devices for Information Technology (MDITR) STC (DMR-0120967)