

ALD Fundamentals

Room On Demand - Session AF4

Growth and Characterization: Surface Science of ALD

AF4-1 Atomic Layer Deposition of Bimetallic Alloy and Work Function Modulation Using Discrete Feeding Method, Ji Won Han, Y. Kim, J. Heo, T. Park, Hanyang University, Korea

For the continuous scaling of semiconductor based nano-electronics, complementary metal oxide semiconductor (CMOS) field effect transistor (FET) also need to be scaled. 3D structures, such as FinFET, have been applied to suppress the short channel effect, and gate all around (GAA) structure which has all four side of channel is surrounded by the gate metal is anticipated as the next generation device structure. Atomic layer deposition (ALD) have been used as deposition technique since deposition of uniform and conformal film on complicated structure is essential and ALD is only way to successfully accomplish the requirements. Also, workfunction materials for both pMOS and nMOS are needed to developed. However, metals having a low work function suitable for nMOS have poor oxidation resistance and thermal stability due to low oxide formation energy. To overcome the limitation, ALD-based metal nitride and metal carbide are being studied as an alternative, but recent researches are still unsatisfactory.

In this work, we demonstrated deposition of bimetallic alloy film of n-type metal and p-type metal *via* ALD, and modulation of the ratio using discrete feeding method (DFM). DFM is an advanced ALD process that improves reaction efficiency, deposition behavior and overall properties of film by removing physisorbed precursors with cut-in purge introduced between subdivided precursor feeding.

It was confirmed that ratio of n-type metal in the film was able to be controlled in the range of 30~50 %, and detailed mechanism of composition modulation through DFM was elucidated based on change of deposition behavior. Resistivity of bimetallic alloy film was applicable to CMOS regardless of the process variation, while slightly changed depending on its composition. Also, effective workfunction of the film was decreased as ratio of n type metal increased, and since the effect from microstructure of the film is added, bimetallic alloy film having workfunction of 4.1 eV that is identical to conduction band minimum of Si was obtained.

AF4-2 Novel ALD Study of TiO₂ and ZrO₂ on Pmma Substrates as Separate and Mixed Oxide Thin Films for Enhanced Biomaterial Functionalization, Mina Shahmohammadi, University of Illinois - Chicago; **B. Nagay, V. Barão,** University of Campinas (UNICAMP), Brazil; **C. Sukotjo, C. Takoudis,** University of Illinois - Chicago

Titanium(IV) oxide (TiO₂) and zirconium oxide (ZrO₂) are well-known materials due to their biocompatibility, hydrophilicity, antimicrobial activity, excellent corrosion resistance, and low cost. Polymethyl methacrylate (PMMA), on the other hand, is a promising polymer with a huge range of applications such as denture base materials. However, its poor surface properties lead to fracture and deformation. The mainline inquiry that is to be explored through this work is how functionalization of PMMA surface would make this polymer more stable and robust in the aggressive oral environment and reduce biofilm formation when used in dental applications. Here, low-temperature Atomic Layer Deposition (ALD) was used to systematically deposit TiO₂ and ZrO₂ as separate and mixed oxide thin films on PMMA substrates. Five groups are deposited and characterized: 1. Non-deposited PMMA (control); 2. TiO₂ deposited PMMA; 3. ZrO₂ deposited PMMA; 4. Mixed TiO₂ and ZrO₂ film with 1:1 thickness ratio of TiO₂:ZrO₂ (TZO1); 5. Mixed TiO₂ and ZrO₂ film with 3:1 thickness ratio of TiO₂:ZrO₂ (TZO3). Tetrakis(dimethylamido)titanium (TDMAT) and tetrakis(dimethylamido)zirconium (TDMAZ) precursors were used to deposit TiO₂ and ZrO₂ thin films, respectively and ozone was used as the oxidizer. The reactor temperature for all the depositions was kept at 120°C and the precursor bubblers of TDMAT and TDMAZ were both kept at 70°C. Spectroscopic ellipsometry was used to measure the metal oxide film thickness on PMMA substrates. The wettability, composition, and surface roughness of each group were examined with water contact angle measurements, x-ray photoelectron spectroscopy (XPS), and Atomic Force Microscopy (AFM), respectively. A systematic ALD study was successfully performed on PMMA to improve its properties for dental applications. The coatings increased the wettability of PMMA surface by over 30%, which is a necessary characteristic for dental applications since a hydrophilic surface has less potential for bacterial attachment. AFM revealed not a significant

change in the surface roughness of PMMA after ALD, which corroborates conformal deposition of the thin films across the substrate. XPS confirmed the presence of each oxide on the surface of PMMA for single oxide films and more importantly, the presence of both oxides for the mixture. The antibacterial activity of each group as well as the studies on the surface roughness and hardness of each group before and after thermal aging will be discussed.

AF4-3 Advanced Atomic Layer Deposition of Metal Oxide Films With Discrete Feeding Method, Jae Chan Park, Hanyang University, Korea; **S. Lee, S. Yoo, J. Lee, K. Dae, J. Jang,** Korea Basic Science Institute, Korea (Republic of); **W. Kim, T. Park,** Hanyang University, Korea

HfO₂, the most widely used gate dielectric layer for semiconductor devices, was grown via atomic layer deposition with discrete feeding method (DFM), and its physical, chemical and electrical properties were studied. In a typical ALD process, all the substrate surface sites hardly react with precursor or reactant molecules, even in adsorption saturated condition, because physisorbed precursor and byproduct molecules screen the subjacent surface sites. The DFM process consists of multiple steps of feeding and purging precursor molecules prior to the reactant feeding/purging step, which can efficiently remove the physisorbed precursor molecules and byproducts.

The assorted properties of HfO₂ thin film were improved with DFM process in various ways; i) increased film density, ii) decreased thickness of the HfO₂/Si interfacial layer, and iii) decreased impurity level in the film, which are crucial for the electrical properties of the high-k dielectrics. These are associated with increased adsorption and filling efficiency of precursor molecules on the substrate surface during initial stage of ALD. The detailed experimental results will be presented.

AF4-4 Study of SiO₂ Growth Mechanism Between a Single SiO₂ and (HfO₂)/(SiO₂) Nanolaminate Formation by ALD Using TDMAS and H₂O Gas, Toshihide Nabatame, WPI-MANA, National Institute for Materials Science, Japan; **M. Inoue, E. Maeda, T. Onaya, M. Hirose, R. Kobayashi,** National Institute for Materials Science, Japan; **A. Ohi,** WPI-MANA, National Institute for Materials Science, Japan; **N. Ikeda,** National Institute for Materials Science, Japan; **K. Tsukagoshi,** WPI-MANA, National Institute for Materials Science, Japan

Recently, Hafnium silicate (HfSiO_x) material has been investigated as dielectrics for AlGaN/GaN high-electron-mobility transistors. To form HfSiO_x, a HfO₂ and SiO₂ (HfO₂)/(SiO₂) nanolaminate film was generally deposited by plasma-enhanced atomic layer deposition (PE-ALD) using tetrakis(dimethylamino)hafnium (TDMAHf) and tris(dimethylamino)silane (TDMAS) and O₂ plasma [1]. This is because the SiO₂ film could not deposit by ALD using TDMAS precursor and H₂O gas. The water gas supply process during ALD sequence is a key point to understand this mechanism of no SiO₂ deposition. In this paper, we study the (HfO₂)/(SiO₂) nanolaminate growth by ALD at 300°C using TDMAHf and TDMAS precursors and H₂O gas. We also discuss about SiO₂ growth mechanism based on data of a single SiO₂ and (HfO₂)/(SiO₂) nanolaminate films.

The growth per cycle (GPC) values of HfO₂ films on p-Si/SiO₂ substrate by ALD with H₂O gas and PE-ALD with O₂ plasma at 300°C using TDMAHf were 0.085 and 0.082 nm/cycle, respectively. On the other hand, the GPC value of SiO₂ film by ALD at 300°C using TDMAS and H₂O gas was ~0 nm/cycle while the GPC value by PE-ALD was 0.043 nm/cycle. Furthermore, the (HfO₂)/(SiO₂) nanolaminate film was deposited by ALD using TDMAHf and TDMAS and H₂O gas. The numbers of ALD cycles (2 and 1) used to deposit the HfO₂ and SiO₂ layers. The GPC of the (HfO₂)/(SiO₂) (2/1) nanolaminate film was found to be 0.25 nm/cycle. This GPC value was closely same as that of the PE-ALD. The Hf:Si ratios in the (HfO₂)/(SiO₂) nanolaminate film were estimated to be 0.59:0.41 and 0.57:0.43 by ALD and PE-ALD, respectively, based on XPS and EDS analysis. In our previous research, we found that the adsorption of the TDMAS precursor strongly depends on the difference in the electronegativities between metal and oxygen of the Metal-O underlayer [2]. Here, we discuss the SiO₂ growth mechanism by ALD using TDMAS and H₂O gas. In the (HfO₂)/(SiO₂) nanolaminate deposition, the TDMAS precursors adsorb on the Hf-O and Si-O areas of the underlayer. Next, the adsorbed TDMAS on the Hf-O area easily react with H₂O gas but no reaction on Si-O area during H₂O gas supply process. This is because TDMAS precursor was partially decomposed on the Hf-O and activated. As a result, the SiO₂ film could be selectively formed on Hf-O area by the oxidation reaction between activated TDMAS precursor and H₂O gas.

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[1] T. Nabatame et al., *Appl. Phys. Express* **12**, 011009 (2019).

[2] E. Maeda et al., *J. Vac. Sci. Technol. A* **38**, 032409 (2020).

AF4-5 Discovery of Crystalline Anatase on Fluorine-Rich Carbon Substrates During Low Temperature ALD of Ultra-Thin TiO₂, Brian Butkus, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee, University of Central Florida

We discover crystalline anatase phase in atomic layer deposition (ALD) of TiO₂ when deposited on a fluorine-rich carbon substrate using titanium(IV) isopropoxide (TTIP) and O₂ plasma. Highly crystalline anatase phase has been detected in films deposited at temperatures as low as 100 °C and with thickness of only ~ 4 nm. On the other hand, TiO₂ films deposited on other forms of carbon substrates, glass and silicon, consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO₂ and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

TiO₂ was deposited on hydrophobic, polytetrafluoroethylene (PTFE) coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store) using a Veeco® Fiji Gen2 ALD system. ALD temperatures were varied from 100 °C to 200 °C and O₂ plasma (300 W) and H₂O were used as oxidants. Target film thickness varied from 4 nm to 22 nm. Raman, Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) were used to characterize the films. Raman spectroscopy data indicated that anatase TiO₂ was observed on all AvCarb GDS2230 substrates using O₂ plasma as an oxidant, including films as thin as 4 nm and, deposited at temperatures as low as 100 °C. When the oxidant is switched to H₂O, the anatase phase is still found, though significantly weaker. An interfacial layer of ALD Al₂O₃ suppresses the growth of anatase phase. XPS data indicates that in films that show anatase TiO₂, Ti-F bond formation occurs at the preliminary deposition stages. This structurally differentiates the amorphous TiO₂ on non-fluorinated substrates which do not show the presence of the Ti-F bond. The presence of fluorine on the surface of the carbon paper acts as a 'structure directing agent' [1-5] where the resulting fluorolysis reaction between TTIP with PTFE drives the TiO₂ crystallizing into anatase film.

Fluorine doped crystallization in Ti-O systems have been reported in sol-gel and hydrothermal approaches to synthesize TiO₂ powders.[6, 7] Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO₂ films. The approach highlighted here can lead to area selective and in situ crystallization of films using suitable surface initiation chemistries.

AF4-6 Thin Films Island Structure Analysis Using X-Ray Photoelectron Spectroscopy Methodology, V. Afanas'ev, **Daniil Selyakov**, Moscow Power Engineering Institute, Russian Federation

Overlayer thickness determination is an important application of X-ray Photoelectron Spectroscopy (XPS). The methodology is based on measurement of substrate and film peak intensities and assumes the presence of a plane-parallel film located on a semi-infinite flat substrate. We will analyze how the XPS signal intensity changes if the film is not a flat homogeneous layer but constitute an island (cluster) structure, which may be energetically favorable for the atoms of the film. Such structures are typical of gold in submonolayer configurations. XPS spectra were measured for three samples (gold films of different thicknesses located on top of silicon substrates) at five different angles and have been interpreted by the straight line approximation model, developed within XPS framework. The effect of a decrease in the value of the effective average coating thickness (d) with a detecting angle increase was observed, when signal is interpreted within flat homogeneous layer coating model. Considering the configuration of an island surface coverage (the simplest model when the half of the silicon surface is covered with plane-parallel islands with a thickness of 2d we can compare the behavior of the theoretical curves showing the dependence of the signal intensity ratio for island and uniform coverage and see that if the flux of photoelectrons is detected at grazing angles, the curves will coincide. The value of the critical angle at which curves coincidence will be determined by the shape of the islands. The presence of an island surface coating can be confirmed by XPS

measurements with an angular resolution and will be accompanied by a decrease in the layer thickness values determined by traditional XPS methodology as the detecting angles approach the grazing angle. The average value of the film thickness (the thickness of an equivalent homogeneous layer) is determined by detecting the XPS signal at angles exceeding the critical angle determined by the island morphology. The simplest model of an island coating makes it possible to qualitatively interpret the effect of a decrease of the effective average coating thickness observed in XPS experiments with an angular resolution.

AF4-9 Thermal and Plasma Enhanced Atomic Layer Deposition of TiO₂ from Amide and Alkoxide Precursors: Growth Characteristics and Photoelectrochemical Performance, **Shane O'Donnell**, F. Jose, K. Shiel, M. Snelgrove, C. McFeely, R. O'Connor, Dublin City University, Ireland

Due to its low cost and suitable band edge positions, Si has been under investigation as a photoanode material for water oxidation for some time¹. However, as a result of poor stability in the oxidative environment, Si is unsuitable for extended use without a protective layer to prevent surface oxidation. Ultra-thin titanium dioxide (TiO₂) films deposited by atomic layer deposition (ALD) have been used as protective coatings and are shown to enhance Si photoanode lifetime by distancing the oxidation reaction from the photoanode surface².

This study details the nucleation, growth chemistry, and photoelectrochemical performance of 2 nm TiO₂ thin films on Si prepared via atomic layer deposition (ALD). We investigate in detail the growth characteristics of films by plasma enhanced and thermal ALD using x-ray photoelectron spectroscopy (XPS), without breaking vacuum. Growth and characterization takes place in a custom designed system with a commercial ALD reactor (Oxford Instruments FlexAL) coupled in vacuum via fast transfer robotic handler allowing for analysis of the nucleation and growth chemistry with half-cycle resolution.

The precursors investigated in this study are titanium isopropoxide (TTIP) and Tetrakis(dimethylamido)titanium (TDMAT). Each precursor material was employed to grow TiO₂ using thermal (H₂O co-reactant) and plasma enhanced (O₂ plasma co-reactant) ALD using the manufacturer's optimized recipes, and the effect of post deposition treatments in reducing and oxidizing ambients was also investigated. The photoelectrochemical performance was monitored to link the impact of precursor and co-reactant choice on surface chemistry and the measured photocurrent.

TiO₂ grown by plasma enhanced ALD results in cleaner films with reduced carbon incorporation from the precursor ligands and titanium exclusively in the 4+ oxidation state. However, despite carbon concentrations of up to 15%, thermally grown films show improved photocurrent. This increased photocurrent is correlated with presence of titanium suboxides observed in the Ti 2p peak of these films. This suggests that oxygen vacancies improve the charge transport through the films. Post deposition annealing in a H₂ ambient is shown to further improve photocurrent in all cases. Thermal annealing in atmosphere leads to even higher photocurrent, enhanced photocurrent stability, and uniform chemistry across all films

1. Hannula, M. et al. *Chem. Mater.* **30**, 1199–1208 (2018)
2. Van De Krol, R. et al. *J. Phys. Chem.* **C121**, 5531–5538 (2017)

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