

ALD Fundamentals

Room On Demand - Session AF3

Precursors and Chemistry: Mechanisms

AF3-1 Titanium Nitride ALD Process Using High Purity Hydrazine: N₂H₄ Reactivity in Gas Phase, Hayato Murata, H. Shimizu, K. Andachi, TAIYO NIPPON SANSO Corporation, Japan; D. Alvarez, J. Spiegelman, RASIRC; K. Suzuki, TAIYO NIPPON SANSO Corporation, Japan

ALD titanium nitride (TiN) with lower resistivity has attracted an attention as DRAM device has higher-aspect-ratio capacitors with its scaling. We reported that ALD TiN films using TiCl₄ and hydrazine (Hy, N₂H₄) has higher GPC, smaller roughness, less chlorine (Cl) impurities, and lower resistivity [1]. Here, we delivered N₂H₄ employing BRUTE Hydrazine (RASIRC, Inc.) which enabled safe delivery of high-purity N₂H₄ gas [2]. In addition to safety and quality of N₂H₄, lab-to-fab scale-up could be efficiently achieved through understanding reaction mechanism of N₂H₄ in the ALD process. In this study, we investigated gas-phase reaction of N₂H₄ in the ALD process and an effect of gas-phase reaction on GPC (growth per cycle).

First, N₂H₄ decomposition was observed above 200°C at 133Pa by quadruple mass spectrometry installed at downstream of a hot-wall tubular reactor. When a gas mixture of 10 sccm N₂H₄ and 240 sccm N₂ flowed through the reactor at 300°C and 400°C (380 cm/s and 450 cm/s), 38% and 55% of N₂H₄ were respectively decomposed before reaching to a substrate (35 cm heated zone before the substrate). Thus, lower-concentration hydrazine is delivered to the substrate in ALD process at higher temperature.

Next, TiN ALD process using TiCl₄/N₂H₄ was performed at 250-400°C. GPCs in TiCl₄/N₂H₄ ALD were found to be 0.42-0.32 Å/cycle while those in TiCl₄/NH₃ ALD were 0.10-0.27 Å/cycle at 250-400°C. Interestingly, the GPC in TiCl₄/N₂H₄ ALD was lower at higher temperature, correlating to the hydrazine concentration estimated by the decomposition study. Further enhancement in throughput could be available by preventing the decomposition of N₂H₄ before reaching to the substrate.

In addition, ALD TiN film using TiCl₄/N₂H₄ likely had as good quality as sputtered TiN. Refractive index (R.I.) of TiCl₄/N₂H₄ film was about 1.68-1.73 at 250-300°C while R.I. of typical sputtered TiN was about 1.66. In contrast, R.I. of TiCl₄/NH₃ film formed at 250-300°C was larger than 2.00 likely due to the formation of titanium oxide whose R.I. is 2.4-2.5. The R.I. results indicate probably that higher-concentration hydrazine have an effect on TiN film quality at lower temperature.

Thus, since TiN ALD using TiCl₄/N₂H₄ has various advantages over that using TiCl₄/NH₃, N₂H₄ is expected to improve both throughput of ALD and quality of nitride ALD films.

[1] D. Alvarez, K. Andachi, G. Tsuchibuchi, K. Suzuki, J. Spiegelman, H. Murata, PRIME2020, G02-1668, 2020.

[2] J. Spiegelman, Daniel Alvarez et al., 18th International Conference on Atomic Layer Deposition, AM-TuP2, 2018.

AF3-2 Mechanistic Insights into the Thermal ALD of Gold: Infrared, Mass Balance, Nucleation, and Epitaxy, P. Liu, Argonne National Laboratory; A. Hock, Illinois Institute of Technology; Alex Martinson, Argonne National Laboratory

An *in situ* microbalance and infrared spectroscopic study of alternating exposures to Me₂Au(S₂CNET₂) and ozone illuminates the organometallic chemistry that allows for the thermal atomic layer deposition (ALD) of gold. The synthetic yield of Me₂Au(S₂CNET₂) was also improved but remains well below 50%, leaving a significant room for improvement of the synthetic method and further motivating the search for related precursors. When we apply deposition conditions optimized for Au ALD growth on itself to oxide substrates the result is a long (300+ cycle) nucleation period, similar to other noble metal ALD processes. After steady-state growth is achieved, the final growth rate (0.14 nm/cycle) is measured to be significantly greater than previously estimated. *In situ* infrared spectroscopy informed by first-principles computation provides insight into the surface chemistry of the self-limiting half-reactions, which are consistent with an oxidized Au surface mechanism. The diethyldithiocarbamate ligand, or remnants thereof, is removed and volatilized by ozone, which is also required for activation of the growing Au surface to endow sufficient activity for reaction with the next Au precursor exposure. This reactivity is significantly reduced, even after ligand removal, upon exposure to a reducing CO atmosphere. X-ray diffraction of ALD-grown gold on silicon, silica, sapphire,

and mica reveals consistent out-of-plane oriented crystalline film growth as well as epitaxially directed in-plane orientation on closely lattice-matched mica at a relatively low growth temperature of 180 °C. A more complete understanding of ALD gold nucleation, surface chemistry, and epitaxy will inform the next generation of low-temperature, nanoscale, textured depositions that are applicable to high surface area supports.

AF3-3 Oxygen Reservoirs in Metal Oxides: Mechanisms of Reactive Species Formation and Transport in Atomic Layer Deposition of Fe₂O₃ and NiO, Joel Schneider, C. de Paula, N. Richey, J. Baker, S. Bent, Stanford University

The ability of atomic layer deposition (ALD) to deposit materials in a uniform, conformal, and controlled fashion hinges on the surface reactions being self-limiting. While this is often the case, not every ALD process is so well-behaved, and understanding and controlling growth mechanisms are critical given the increasing material demands of ALD. Previous work has shown that the ALD reactions of iron (III) oxide are not limited to the substrate surface but rather involve sub-surface mechanisms. This work uses *in situ* techniques to investigate these mechanisms of ALD growth and the role of active species transport through the film, using ozone-based ALD of Fe₂O₃ and NiO as comparative case studies.

Iron and nickel oxide thin films were deposited using metallocene precursors with ozone, and film thickness was monitored using ellipsometry. *Ex situ* angle-resolved X-ray photoelectron spectroscopy (XPS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) revealed subsurface changes and in some cases the formation of a layer of superstoichiometric oxygen near the film surface that correlates with O₃ exposure. Quartz crystal microbalance and *in vacuo* XPS were then employed to probe the sub-surface storage of superstoichiometric oxygen. Oxygen is present in two different chemical states within Fe₂O₃, and it was found the introduction of superstoichiometric oxygen with O₃ and its consumption by TBF track most strongly with the lower binding energy state of oxygen. Comparisons to the behavior of the NiO process were also made, and through *in situ* quadrupole mass spectrometry to examine gaseous reaction byproducts, stored oxygen is observed to be in a reactive form that actively participates in ALD half-reactions.

The storage and transport of oxygen through the film was also investigated. GIWAXS measurements show sub-surface transport of oxygen correlates with the reorientation of the crystalline domains such that the lattice axis with most facile oxygen diffusion preferentially orients parallel to the direction of oxygen transport. Trends regarding the degree of crystallinity and domain orientation were also observed. These studies shed light on the fundamental chemical mechanisms behind reactive oxygen species in metal oxide ALD, with additional work suggesting these mechanisms can be leveraged in enhancing growth in both ternary ALD and catalytically activated ALD, posing implications for the broader class of ozone- and oxygen plasma-based ALD processes.

AF3-4 Nonaqueous Atomic Layer Deposition of Zinc Oxide Using Diethylzinc and Ethanol, Miso Kim, E. Shin, J. Hwang, B. Shong, Hongik University, Korea (Republic of)

Zinc oxide (ZnO) is a transparent wide-band gap semiconductor that can be used in various fields such as thin film transistors (TFTs), gas sensors, and catalysts. Atomic layer deposition (ALD) of ZnO is widely applied due to the ability to form conformal high-quality thin films at the Angstrom level. Most previous studies on ZnO ALD utilized a few well-known precursors and reactants such as diethylzinc (DEZ), dimethylzinc (DMZ), H₂O and O₃. However, O₃ and H₂O oxidants have relatively strong reactivity, so that they are not suitable for substrates that are easily oxidized or reactive with water. Therefore, development of nonaqueous alternative ALD process for ZnO is desired. In this study, we introduce ALD of ZnO using ethanol as a nonaqueous oxidant. Density functional theory (DFT) results indicated that the β-H of the ethanol molecule is crucial in the reaction mechanism for removal of C moieties during the oxidant pulse. Using DEZ as Zn precursor, a typical ALD growth behavior and highly conformal films of ZnO were obtained between 100-300 °C. Compared to the ALD ZnO films deposited with H₂O, nonaqueous-ALD ZnO films showed similar C content, lower crystallinity, higher conductivity, and higher mobility.

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