

ALD Fundamentals

Room On Demand - Session AF5

Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD

AF5-1 Conformal Atomic Layer Deposition of Ultra-Thin Conductive Silver Films, S. Wack, P. Lunca Popa, N. Adjeroūd, C. Vergne, **Renald Leturcq**, Luxembourg Institute of Science and Technology (LIST), Luxembourg

In the fabrication of microelectronic devices, which include DRAM capacitors, transistors, and back-end-of line (BEOL) interconnects, silver (Ag) is of particular interest due to its low electrical resistivity and low residual stress compared to Cu, and allows downscaling to less than 100 nm without a considerable increase in resistivity [1]. While the deposition of highly uniform and conformal conductive ultra-thin Ag films is of great interest due to the miniaturization and three-dimensional architecture of semiconductor devices [2,3], there is currently no reliable Ag deposition method providing conformal ultra-thin conductive films, mainly due to the island deposition mode of standard non line-of-sight deposition methods, including atomic layer deposition (ALD) [3,4].

We have investigated the conformal deposition of silver films by plasma-enhanced atomic layer deposition (PEALD) using large horizontal aspect ratio (LHAR) structures from Pillarhall®, including a new process in two steps allowing the conformal deposition of ultra-thin conductive silver films [5]. While the standard PEALD process shows an exponential decrease of the deposited material in the LHAR structure, presumably limited by the recombination of plasma radicals on the walls, our new approach demonstrates high conformality of the deposited film on complex lateral high aspect ratio structures (up to 100). Moreover the obtained layer remains continuous inside the structure.

This new processing approach opens a very promising route for the use of ultra-thin silver films for electronic and optoelectronic applications, and could be extended to other metals deposited from metal-organic precursors, in particular copper and gold, for which the deposition using chemical vapor based methods is a very active field.

[1] Amusan et al., *J. Vac. Sci. Technol.* **A2016**, *34*, 01A126

[2] Cremers et al., *Appl. Phys. Rev.* **2019**, *6*, 021302

[3] Hagen et al., *Appl. Phys. Rev.* **2019**, *6*, 041309

[4] Wack et al., *J. Phys. Chem.* **C2019**, *123*, 27196

[5] Wack et al., *ACS Appl. Mater. Interfaces* **2020**, *12*, 36329

AF5-2 Toolbox for ALD Process Development on High Surface Area Powders, **Kristian Knemeyer**, BasCat - UniCat BASF JointLab, TU Berlin, Germany; R. Baumgarten, BasCat - UniCat BASF Jointlab, TU Berlin, Germany; P. Ingale, R. Naumann d'Alnoncourt, BasCat - UniCat BASF JointLab, TU Berlin, Germany; M. Driess, Technical University of Berlin, Germany; F. Rosowski, BASF SE, Process Research and Chemical Engineering, Germany

Atomic layer deposition (ALD) is an industrially applied technique for thin film deposition with its origin in microelectronics.¹ Over the course of the past 50 years a wide variety of elements and combinations thereof were deposited via ALD.² However, the vast majority of processes targets flat substrates rather than powders. For ALD on powders, different reaction conditions are required and need to be identified for ALD to be applicable to high surface area powders. This work shows two setups in detail, which enhance the ALD process development for powders.³ The first setup is capable of directly measuring the vapor pressure of a given precursor to pre-select promising precursors and their ideal saturation temperature. Afterwards, the second setup, consisting of four parallel reactors with individual temperature zones, is used to screen the optimal ALD temperature window in a time efficient way. Identifying the precursor saturation temperature beforehand and subsequently performing the first ALD half cycle in the parallel setup at four different reactor temperatures simultaneously will drastically reduce process development times. Validation of both setups is shown for the well-known ALD precursors trimethylaluminum to deposit aluminum oxide and diethyl zinc to deposit zinc oxide, both on amorphous silica powder. It can be shown that ALD on high surface area powders requires lower reactor temperatures than ALD on flat substrates. Furthermore, vapor pressures measurements of metal acetylacetonates revealed the need for elevated precursor temperatures

for sufficient vapor pressures. There, to achieve reasonable vapor pressures of >10 mbar saturation temperatures of 100 °C are often needed.

1G. N. Parsons, J. W. Elam, S. M. George, S. Haukka, H. Jeon, W. M. M. (Erwin) Kessels, M. Leskelä, P. Poedt, M. Ritala and S. M. Rosnagel, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, 2013, **31**, 050818.

2R. L. Puurunen, *J. Appl. Phys.*, 2005, **97**, 121301.

3K. Knemeyer, R. Baumgarten, P. Ingale, R. N. d'Alnoncourt, M. Driess and F. Rosowski, *Rev. Sci. Instrum.*, 2021, 1–24.

AF5-3 Tunable ALD Infiltration into Ultra-High-Aspect-Ratio Aerogels Enabled by Process Modeling for High-Temperature Solar Thermal Applications, **Andrew J. Gayle**, Z. Berquist, University of Michigan, Ann Arbor; Y. Chen, University of Michigan; A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta, University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels helps enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. In particular, SiO₂ aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally coat SiO₂ aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. In order to minimize precursor waste during the long diffusion times necessary to conformally coat the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an “exposure step”, allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Building on previous work by Gordon [2] and Yanguas-Gil [3], our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD coating process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. After deposition, the AMs showed enhanced infrared light absorption while maintaining high visible light transparency after only one cycle of ALD Al₂O₃. The ALD-coated AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO₂ nanoparticle surface. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO₂ backbone and deposited Al₂O₃ film, as shown using XPS measurements. This combination of properties makes the ALD-coated AMs a promising transparent insulating material (TIM) for CST applications.

[1] A. Gayle, Z. Berquist et al. *Submitted 2021*.

[2] R. G. Gordon et al. *Chem. Vap. Depos.* **2003**, *9* (2), 73-78.

[3] A. Yanguas-Gil et al. *Chem. Vap. Depos.* **2012**, *18* (1-3), 46-52.

AF5-4 Enhanced Throughput of High-Aspect-Ratio Atomic Layer Deposition Using Trimethylaluminum and Hydrogen Peroxide, **Hideharu Shimizu**, T. Mizuno, Taiyo Nippon Sanso, Japan; D. Alvarez, J. Spiegelman, RASIRC

Aluminum oxide (Al₂O₃) ALD has been studied and used for the mass production of devices. However, its long process time for high-aspect-ratio (HAR) structures is a critical drawback [1]. In this study, the reaction mechanism of Al₂O₃ ALD using trimethylaluminum (TMA) and H₂O₂/H₂O mixture [2] or H₂O was investigated; our results indicate that H₂O₂ could be purged more quickly than other reactants. Here, we used RASIRC's Peroxidizer™ to deliver the H₂O₂/H₂O mixture at a reproducible concentration. We demonstrated that the H₂O₂/H₂O mixture can shorten the purge period after a reactant feeding, leading to higher-throughput Al₂O₃ ALD for a HAR structure.

First, quantum chemical calculations and an exhaust gas analysis based on quadruple mass spectrometry were employed to study the reaction mechanism of ALD using the H₂O₂/H₂O mixture. A surface reaction between H₂O₂ and adsorbed TMA is expected to generate CH₃OH, which is thermodynamically favorable since the calculated reaction energy (ΔH) is -

On Demand

256 kJ/mol (Fig. 1). In addition, a surface reaction between H_2O and adsorbed TMA is expected to generate CH_4 , for which the calculated ΔH is estimated to be -40 kJ/mol. In fact, using $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, the exhaust gas analysis identified CH_3OH during reactant feeding step in ALD (Fig. 2a). CH_4 , but not methanol, was observed in ALD using H_2O (Fig. 2b). These results indicate that the surface reaction in ALD using $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ is irreversible, while that using H_2O can be reversed to regenerate H_2O during the subsequent purge period.

Next, Al_2O_3 ALD was performed on a HAR structure (A/R ~ 100) using $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture, H_2O , or O_3 with different purge periods and a reactant feed period of 10 s (Fig. 3a). Under these conditions, the conformality of the ALD was controlled by TMA diffusion. Conformality is generally worsened with a shorter purge period due to the formation of a reactive intermediate during precursor feeding [3]. In fact, when H_2O or O_3 was used as a reactant, ALD with the shorter purge period provided films with poorer conformality (Fig. 3b, c). However, using the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture with ALD reduced the purge period from 10 to 5 s without reducing conformality (Fig. 3d). This likely occurred because the irreversible reaction noted above prevented regeneration of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ during the purge period. Thus, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ is a promising reactant to enhance the throughput of ALD processes.

[1] F. Pierrat and J. Vitiello, *J. Vac. Sci. Technol. B*, 2016, Vol. 34, p.021202.

[2] Adam Hinckley et al., AVS Annual Meeting 2017. p.94.

[3] G. Yuan et al., *Jpn. J. Appl. Phys.*, 2019, Vol. 58, p.075505.

Author Index

Bold page numbers indicate presenter

— A —

Adjeroud, N.: AF5-1, **1**

Alvarez, D.: AF5-4, **1**

— B —

Baumgarten, R.: AF5-2, **1**

Berquist, Z.: AF5-3, **1**

Bielinski, A.: AF5-3, **1**

— C —

Chen, Y.: AF5-3, **1**

— D —

Dasgupta, N.: AF5-3, **1**

Driess, M.: AF5-2, **1**

— G —

Gayle, A.: AF5-3, **1**

— H —

Hill, A.: AF5-3, **1**

Hoffman, J.: AF5-3, **1**

— I —

Ingale, P.: AF5-2, **1**

— K —

Knemeyer, K.: AF5-2, **1**

— L —

Lenert, A.: AF5-3, **1**

Leturcq, R.: AF5-1, **1**

Lunca Popa, P.: AF5-1, **1**

— M —

Mizuno, T.: AF5-4, **1**

— N —

Naumann d'Alnoncourt, R.: AF5-2, **1**

— R —

Rosowski, F.: AF5-2, **1**

— S —

Shimizu, H.: AF5-4, **1**

Spiegelman, J.: AF5-4, **1**

— V —

Vergne, C.: AF5-1, **1**

— W —

Wack, S.: AF5-1, **1**