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UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

MICRON TECHNOLOGY, INC.
Petitioner

v.

PRESIDENT AND FELLOWS OF HARVARD COLLEGE
Patent Owner

Case No. IPR2017-00664
Patent No. 8,334,016

PATENT OWNER'S RESPONSE

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2101	Declaration of Wayne L. Gladfelter, Ph.D. in Support of Patent Owner's Preliminary Response ("Gladfelter Decl.")
2102	A.C. Jones et al., <i>MOCVD and ALD of High-K Dielectric Oxides Using Alkoxide Precursors</i> , 12 Chem. Vap. Deposition 83-98 (2006) ("Jones")
2103	R. M. Fix et al., <i>Synthesis of Thin Films by Atmospheric Pressure Chemical Vapor Deposition Using Amido and Imido Titanium (IV) Compounds as Precursors</i> , 2 Chem. Mater. 235-41 (1990) ("Fix")
2104	K. Ishihara et al., <i>Characterization of CVD-TiN Films Prepared with Metalorganic Source</i> , 29 Jpn. J. Appl. Phys. 2103-05 (1990) ("Ishihara")
2105	L.H. Dubois et al., <i>Infrared Studies of Surface and Gas Phase Reactions Leading to the Growth of Titanium Nitride Thin Films from Tetrakis(dimethylamido)titanium and Ammonia</i> , 139 J. Electrochem. Soc'y 3603-09 (1992) ("Dubois '92")
2106	L.H. Dubois, <i>Model Studies of Low Temperature Titanium Nitride Thin Film Growth</i> , 13 No. 8 Polyhedron 1329-36 (1994) ("Dubois '94")
2107	Excerpt of U.S. Patent No. 7,507,848 File History, Gordon Decl. Aug. 12, 2008 ("848 FH")
2108	Excerpt of U.S. Patent No. 7,507,848 File History, Gordon Decl. Aug. 12, 2008, Exhibit B, <i>2000 International Technology Roadmap for Semiconductors</i> ("ITRS")
2109	N. Herlin et al., <i>Investigation of the Chemical Vapor Deposition of Silicon Carbide from Tetramethylsilane by in Situ Temperature and Gas Composition Measurements</i> , 96 J. Phys. Chem. 7063-72

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2110	K. Bechamp et al., <i>A Combined Electron Paramagnetic Resonance and Fourier Transform Infrared Study of the Co(C₆H₆)_{1,2} Complexes Isolated in Neat Benzene or in Cryogenic Matrixes</i> , 110 J. Phys. Chem. 6023-31 (2006) (“Bechamp”)
2111	G.V.D. Tiers, <i>Proton Nuclear Resonance Spectroscopy. I. Reliable Shielding Values by “Internal Referencing” with Tetramethylsilane</i> , 62 J. Phys. Chem. 1151-52 (1958) (“Tiers”)
2112	Hämäläinen et al., <i>Atomic Layer Deposition and Characterization of Aluminum Silicate Thin Films for Optical Applications</i> , 158 J. Electrochem. Soc’y 15-21 (2011) (“Hämäläinen”)
2113	F. Zaera, <i>The Surface Chemistry of Thin Film Atomic Layer Deposition (ALD) Processes for Electronic Device Manufacturing</i> , 18 J. Mater. Chem. 3521-26 (2008) (“Zaera”)
2114	Sugiyama et al., <i>Low Temperature Deposition of Metal Nitride by Thermal Decomposition of Organometallic Compounds</i> , 122 J. Electrochem. Soc’y, Solid-State Sci. & Tech. 1545-49 (1975) (“Sugiyama”)
2115	J. Provine & M. Rincon, M., <i>Atomic Layer Deposition: Introduction to the Theory and Cambridge Nanotech Savannah & Fiji</i> , Stanford University (2012) https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/ald-tutorials . (“Provine”)
2116	Gordon, R.G., et. al., <i>Volatile Liquid Precursors for the Chemical Vapor Deposition (CVD) of Thin Films Containing Tungsten</i> , 612 Mat. Res. Soc. Symp. Proc. D9.12.1-12.6 (2000)
2117	Excerpt of No. 8,334,016 File History, Notice of Allowance, Oct. 10, 2012 (“’016 FH”)
2118	European Patent Register, EP1067595, <i>Liquid Precursor Mixtures for Deposition of Multicomponent Metal Containing Materials</i> (Apr. 20, 2017),

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	https://register.epo.org/application?number=EP00114321&lng=en&tab=main .
2119	U.S. Patent No. 6,238,734, Liquid Precursor Mixtures for Deposition of Multicomponent Metal Containing Materials

New

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2120	Declaration of Wayne L. Gladfelter, Ph.D. in Support of Patent Owner Response (“Gladfelter 2d. Decl.”)
2121	Deposition Transcript of Sanjay Banerjee and Errata Sheet (“Banerjee Tr.”)
2122	2 M.L.H. Green et al., <i>Organometallic Compounds: The Transition Elements</i> (3d ed.1968) (“Green”)
2123	Tuomo Suntola, <i>Atomic Layer Epitaxy</i> , 4 Materials Sci. Reps. 261 (1989) (“Suntola III”)
2124	1 Irving Wender & Piero Pino, <i>Organic Synthesis Via Metal Carbonyls</i> (1968) (“Wender”)
2125	M.E. Gross et al., <i>Organometallic Chemical Vapor Deposition of Cobalt and Formation fo Cobalt Disilicide</i> , 6 J. Vacuum Sci. & Tech. 1548 (1988) (“Gross”)
2126	G.J.M. Dormans et al., <i>OMCVD of Cobalt and Cobalt Silicide</i> , 114 J. Crystal Growth 364 (1991) (“Dormans”)
2127	Matti Putkonen, <i>Atomic Layer Deposition of Nanostructured Materials: Precursors for ALD Processes</i> , 41-50 (Nicola Pinna & Mato Knez eds., 2012) (“Putkonen”)
2128	Ville Miikkulainen et al., <i>Crystallinity of Inorganic Films Grown by Atomic Layer Deposition: Overview and General Trends</i> , 113 J. Appl. Phys. 021301 (2013) (“Miikkulainen”)

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2129	Satoshi Kamiyama et al., <i>Electrical Properties of Ultrathin HfO₂ Films for Replacement Metal Gate Transistors, Fabricated by Atomic Layer Deposition Using Hf(N(CH₃)(C₂H₅))₄ and O₃</i> , 87 Appl. Phys. Letters 132904 (2005) (“Kamiyama”)
2130	A. Katz et al., <i>Properties of Titanium Nitride Thin Films Deposited by Rapid-Thermal-Low-Pressure-Metalorganic-Chemical-Vapor-Deposition Technique Using Tetrakis (Dimethylamido) Titanium Precursor</i> , 70 J. Appl.Phys. 3666 (1991) (“Katz”)
2131	Alex B.F. Martinson et al., <i>Atomic Layer Deposition of Fe₂O₃ Using Ferrocene and Ozone</i> , 115 J. Phys. Chem. C. 4333 (2011) (“Martinson”)
2132	Jonathan R. Scheffe et al., <i>Atomic Layer Deposition of Iron (III) Oxide on Zirconia Nanoparticles in a Fluidized Bed Reactor Using Ferrocene and Oxygen</i> , 517 Thin Solid Films 1874 (2009) (“Scheffe”)
2133	Timothy P. Holme & Fritz B. Prinz, <i>Atomic Layer Deposition and Chemical Vapor Deposition Precursor Selection Method Application to Strontium and Barium Precursors</i> , 111 J. Phys. Chem. A 8147 (2007) (“Holme”)
2134	Thomas Waechtler et al., <i>Copper Oxide Films Grown by Atomic Layer Deposition from Bis(tri-n-butylphosphane) copper(I) acetylacetonate on Ta, TaN, Ru, and SiO₂</i> , 156 J. Electrochem. Soc’y H453 (2009) (“Waechtler”)
2135	T. Kodas & M. Hampden-Smith, <i>The Chemistry of Metal CVD</i> (1994) (“Kodas”)
2136	Lee et al., <i>Mass Production Worthy HfO₂-Al₂O₃ Laminate Capacitor Technology using HfLiquid Precursor for Sub-100nm DRAMs</i> , Electron Devices Meeting, IEDM December 8-11, 2002 (“Lee”)
2137	D.M. Hausmann et al., <i>Atomic Layer Deposition of Hafnium and Zirconium Oxides Using Metal Amide Precursors</i> , 14 Chem. Mater.

Exhibit No.	Exhibit Description
	4350-4358 (2002) (“Hausmann”)

I. INTRODUCTION

Pursuant to 37 C.F.R. § 42.120, the Patent Owner, President and Fellows of Harvard College (“Harvard”) hereby submits this Response to the Petition seeking *inter partes* review of U.S. Patent No. 8,334,016 (“the ’016 Patent”), and to the grounds for which trial was instituted in the Institution Decision dated July 24, 2017 (Paper 11, “Institution Decision”). This filing is timely under 35 U.S.C. § 313-319 and 37 C.F.R. § 42.120, because it was filed by October 30, 2017, in accordance with the parties’ joint notice of stipulation to amend the scheduling order. *See* Paper 16.

The Institution Decision instituted trial as to claims 1, 2, 7, 8, and 10 of the ’016 Patent (the “Challenged Claims”). With respect to claims 1, 2, 7, and 10, trial was instituted on grounds under 35 U.S.C. § 103 as being obvious over U.S. Patent No. 6,537,613, “Process For Metal Metalloid Oxides And Nitrides with Compositional Gradients” (Ex. 1005, “Senzaki”) in view of an article by J. Min, entitled “*Atomic Layer deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethyldamino)-Titanium and Ammonia*” (Ex. 1006, “Min”). With respect to claim 8, trial was instituted on grounds under 35 U.S.C. § 103 as being obvious over Senzaki in view of Min and Korean Patent KR0156980 “Compound

for the Deposition of Metal Nitride Thin Film and Deposition Method Thereof”
(Ex. 1007, “Shin”).

Patent Owner submits that the Petitioner has failed to meet its burden to prove invalidity of any of the Challenged Claims. As discussed in detail below, Petitioner has failed to prove that Senzaki in view of Min suggests or renders obvious the processes recited by the Challenged Claims. As the Board recognizes “Senzaki does not disclose an explicit example of forming a metal oxide layer using a metal alkylamide in an ALD process.” Institution Decision at 10. Further, “Petitioner concedes that Senzaki does not explicitly state that the depositions of the first precursor and the second reactant are self-limiting.” Institution Decision at 9 (citing Petition at 31-35). In an attempt to cure the deficiencies with Senzaki, Petitioner argues that one of ordinary skill would modify Senzaki’s process in view of Min. However, as discussed in more detail below, a POSA would not have combined the teachings of Senzaki and Min to arrive at a self-limiting ALD process using a metal alkylamide precursor to deposit a metal oxide film. Petitioner admits that Senzaki and Min do not disclose the subject matter of Claim 8. Petition at 45. Specifically, Petitioner indicates that Senzaki and Min do not disclose tetrakis(ethylmethyamido)zirconium. *Id.* However, Shin does not cure the deficiencies noted above with respect to Senzaki and Min.

As a result, and for the reasons discussed more fully below, Petitioner cannot meet its burden to prove the invalidity of the challenged claims.

II. THE '016 PATENT

A. Overview of The '016 Patent

The title of the '016 Patent is “Vapor Deposition of Metal Oxides, Silicates and Phosphates, and Silicon Dioxide.” The inventions claimed by the '016 Patent include novel processes and materials for deposition of thin films that contain metal oxides, silicates, metal phosphates, or silicon dioxide. Ex. 1001 at 1:22-28; Gladfelter Decl. at ¶46.

The claimed inventions are directed to atomic layer deposition (“ALD”). Gladfelter Decl. at ¶47; *see also* Ex. 1001 at 30:9-44; Ex. 2117, Banerjee Tr. at 21:20-25. ALD is a process by which certain thin films for microelectronics are produced. Gladfelter Decl. at ¶47; *see also* Ex. 1001 at 1:48-54. ALD requires a number of process steps, and includes the use of at least two chemical precursors with appropriate reactive properties. Gladfelter Decl. at ¶47; *see also* Ex. 1001 at 20:56-21:8. The chemical precursors used in an ALD process should not leave behind elements that are deleterious to the properties of the film. Gladfelter Decl. at ¶47; *see also* Ex. 1001 at 1:55-2:3. These problems have been found with the use of precursors such as metal halides and silicon alkoxides. *Id.*

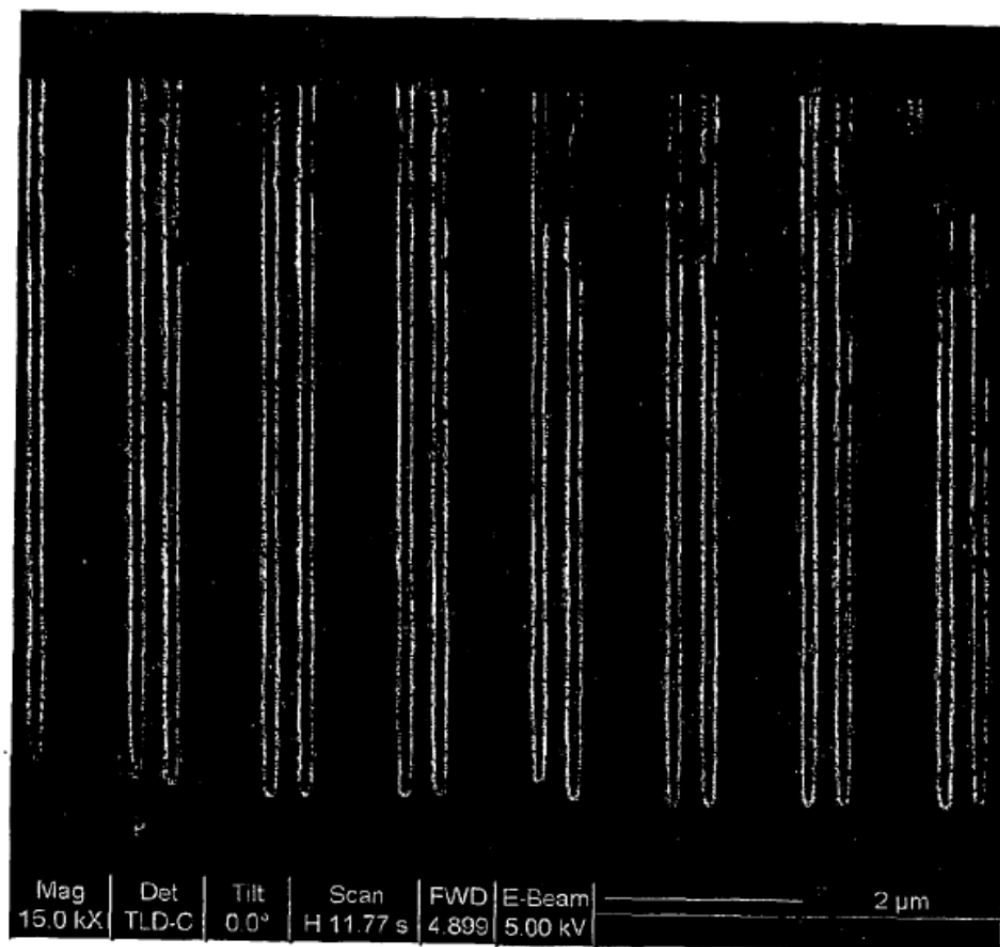
Additional problems were encountered when forming dielectric materials in deep trench structures, such as dynamic random access memory (DRAM) devices. Gladfelter Decl. at ¶48 (citing Ex. 1054, ITRS Roadmap at 3, Ex. 1043, SST at 6-7; Ex. 2107, '848 FH at 2-4; Ex. 1003, '663 Banerjee Decl. at ¶69).

No solution for coating surfaces of deep trenches with high dielectric materials was even expected until 2008. Gladfelter Decl. at ¶49; *see also* Ex. 2107 at 2-4, Ex. B. In fact, near the effective filing date of the present application, a group of semiconductor industry experts believed that the high-dielectric material problem would not be solved for at least another eight years. Gladfelter Decl. at ¶49; *see also* Ex. 2107 at 2-4, Ex. B.

The ALD processes and materials claimed by the '016 Patent solve some of the problems associated with the production of microelectronic devices at smaller sizes, such as the formation of dielectric coatings in deep trench structures. Gladfelter Decl. at ¶50; *see also* Ex. 1001 at FIG. 3, 2:14-52, 19:41-48, 6:33-35, 27:18-35, 30:9-44.

Figure 3 of the '016 Patent, shown below, is a cross-sectional scanning electron micrograph of holes in a silicon wafer uniformly coated with hafnium dioxide using one embodiment of the invention. Ex. 1001 at 6:33-35; Gladfelter Decl. at ¶51.

Fig. 3



The '016 Patent applicants noted the surprising result of the claimed use of metal alkylamide precursors in ALD to form highly uniform films of metal oxide in holes with very high aspect ratios. Gladfelter Decl. at ¶52 (citing Ex. 1001 at 19:41-48).

B. State of the Art of the Time of the '016 Patent

1. Precursor Chemistry in ALD Processes was Known to be Unpredictable

The scope of the claimed inventions falls within the field of chemistry, which has long been acknowledged to be unpredictable. *See Boston Scientific Corp. v. Johnson & Johnson, Inc.*, 679 F. Supp.2d 539, 557 (D. Del. 2010). Chemistry is an experimental science, meaning that one cannot predict the outcome of an experiment without actually carrying out the experiment in the laboratory. *See, e.g., In re Carleton*, 599 F.2d 1021, 1026 (C.C.P.A. 1979) (“Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting precisely how a given compound will behave.”); *Schering Corp. v. Gilbert*, 153 F.2d 428, 433 (2d Cir. 1946) (referring to an area of chemistry as an experimental science with results that “are often uncertain, unpredictable and unexpected.”).

A person of ordinary skill in the art (POSA) would understand that the precursor chemistry involved in the formation of a metal film via an ALD process is unpredictable. Gladfelter Decl. at ¶110. In the late 1990s, at the time of the invention, it was understood that it was difficult to predict without extensive

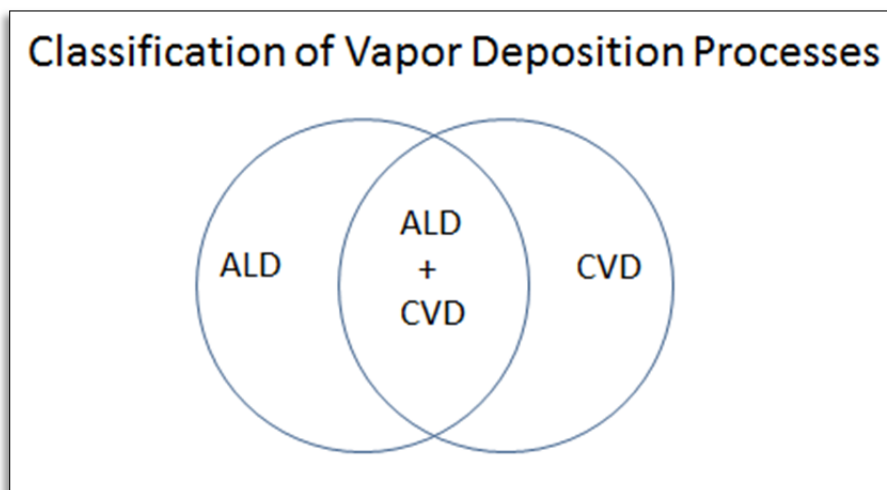
experimentation whether a precursor could be used in an ALD reaction to form a desired film. Gladfelter Decl. at ¶111; *see also, e.g.*, Ex. 1033, Goodman at 8.

Those of ordinary skill in the art recognized that even pre-process calculations regarding theoretical ALD process reactions are not sufficient to determine whether an ALD process will be successful. *See* Gladfelter Decl. at ¶111; Ex. 1008, Leskelä I at 20. For example, those of skill in the art understood that, while useful, thermodynamic considerations of the reactions prior to experimental work cannot be used to predict with any reasonable degree of confidence whether film growth will occur. *See* Gladfelter Decl. at ¶111; Ex. 1008 at 20; *see also* Banerjee Tr. at 89:14-90:26 (acknowledging that “chemistry is a science and at the end of the day, you do want to do experiments to make sure that what a strong suggestions based on thermodynamics are borne out in the lab”).

Additionally, in the late 1990s, those of skill in the art understood the importance of, and difficulties with precursor chemistry in ALD processes, and understood that further development and testing was necessary. Gladfelter Decl. at ¶113; *see also* Ex. 1012, Leskelä II at 21.

Those of skill in the art further understood that precursor chemistry for CVD processes is also unpredictable, and that due to the significant differences between, and unpredictable nature of ALD and CVD processes, precursors that may be suitable for one process, are not necessarily suitable for the other. *See* Gladfelter

Decl. ¶¶115-21; Gladfelter 2d. Decl. at ¶26; Banerjee Tr. at 66:18-67:7 (“Yes, there can be some where CVD precursors may not work for ALD, that's correct.”), 74:15-23 (“Not all CVD precursors may work for ALD. . .”) In fact, in 2006, a study concluded that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD. Gladfelter Decl. ¶119; *see also* Ex. 2102, Jones.



The diagram above visually depicts how a POSA would have understood the relationship of precursors used in ALD and CVD processes. *See* Gladfelter Decl. at ¶116. A person of ordinary skill would understand that, while there is overlap, not all precursors are suitable for both ALD and CVD. *See* Gladfelter Decl. at ¶¶115-121; Gladfelter 2d. Decl. at ¶27; Banerjee Tr. at 66:18-67:7, 74:15-23.

2. Deposition of Metal Alkylamides Was Understood to Lead to Unsuitable Levels of Contamination in Oxide Films

At the time of the inventions, research into the deposition of metal alkylamides was known to lead to unsuitable levels of contamination in oxide films. *See* Gladfelter Decl. at ¶¶122-129. Based on this research, those of ordinary skill in the art would have expected that the use of metal alkylamides in an ALD process to produce a metal oxide film would have also led to unsuitable levels of contamination, in the form of carbon and nitrogen impurities, in the resulting film. *See id.*

Particularly, those of ordinary skill in the art would have considered an ALD process to be similar to a CVD process known as “single source CVD,” in the way a precursor would interact with a heated substrate in a deposition chamber. Gladfelter Decl. at ¶124. Single source CVD is a CVD process using only one precursor compound. *Id.* In single source CVD, a single precursor is introduced into the deposition chamber, usually with a carrier gas, to form a film on a heated substrate. *Id.* Similarly, in an ALD process, precursors are alternately introduced into the deposition chamber, such that only a single precursor is introduced into the deposition chamber at a time. *Id.* As discussed in Dr. Gladfelter’s declaration, research into single source CVD using metal alkylamide precursors produced films with unsuitable levels of contamination. *See id.* at ¶¶122-128.

Additionally, when depositing a metal oxide film, as opposed to metal nitride film, a reactant with an oxygen source is necessary. *See id.* at ¶130. Ammonia (NH₃), which was employed in the Dubois '94 to reduce carbon contamination, does not provide an oxygen source and would not be a suitable reactant for the formation of an oxide film. *Id.* Further, when depositing an oxide film, not only carbon but also nitrogen are sources of contamination in the resulting film. *Id.* at ¶130. Metal alkylamides are characterized as “amides” due to their bonds with nitrogen and, can act as a source of nitrogen contamination. *See id.*

As such, at the time of the claimed inventions, those of ordinary skill in the art would have considered the use of a metal alkylamide in an ALD process to produce a metal oxide film to be particularly susceptible to unsuitable levels of contamination. *See Gladfelter Decl.* at ¶¶122-130.

III. CLAIM CONSTRUCTION AND ORDINARY SKILL IN THE ART

A. Claim Construction

In an *inter partes* review, claim terms in an unexpired patent are interpreted according to their broadest reasonable construction in light of the specification of the patent in which they appear. 37 C.F.R. § 42.100(b); *Office Patent Trial Practice Guide*, 77 Fed. Reg. 48,756, 48,766 (Aug. 14, 2012). Under this standard, a claim term is given its ordinary and customary meaning as it would be

understood by one of ordinary skill in the art. *In re Translogic Tech., Inc.*, 504 F.3d 1249, 1257 (Fed. Cir. 2007); *TRW Automotive U.S., LLC v. Magna Electronics, Inc.*, IPR2015-00949, Paper 7 at 9 (Sep. 17, 2015). Patent Owner proposes that claim terms should be given their ordinary meaning for the purpose of this response without prejudice.

B. A Person of Ordinary Skill In The Art

Petitioner alleges that a hypothetical person of ordinary skill in the art (“POSA”), with respect to the technology described in the ’016 Patent, at the time of the invention, “would be a person with at least a Bachelor of Science degree in electrical engineering, chemical engineering, chemistry, physics, materials science, or a closely related field, along with at least 5 years of experience in developing vapor deposition processes to form thin films. An individual with an advanced degree in a relevant field would require less experience in developing vapor deposition processes to form thin films.” Petition at 21. Patent Owner applies Petitioner’s proposed POSA standard for the purposes of this proceeding.

IV. SUMMARY OF ALLEGED PRIOR ART

A. U.S. Patent No. 6,537,613, “Process For Metal Metalloid Oxides And Nitrides with Compositional Gradients” (“Senzaki”)

Senzaki is directed to a process for deposition of a multiple metal and metalloid compound layer with a compositional gradient of the metal and metalloid in the layer on a substrate of an electronic material by varying the temperature of

deposition from a first temperature to a second distinct temperature. *See* Senzaki at Abstract, 2:33-57, 3:40-46, 6:27-34; Gladfelter Decl. at ¶83, 171; Banerjee Tr. at 102:3-14; Institution Decision at 6 (“In the process of Senzaki, . . . [t]he temperature of the deposition is [] varied by at least 40° C to deposit a metal/metalloid compound layer have a compositional gradient.”)

As Petitioner provides:

According to Senzaki, when fabricating gate oxides, interlayer dielectrics, and other electronic materials “in the field of electronic materials for device fabrication,” “it is desirable to have materials which have a varying compositional gradient of mixed metals or metal/metalloid composition in either oxide, oxynitride or nitride form.” [Senzaki], 2:18-23. However, Senzaki asserts that the prior art had not developed a reliable method for controllably producing such a compositional gradient. *Id.*, 2:24-28.

Petition at 22. “Senzaki addresses the purported failure of the prior art to provide a desirable method for controllably producing a mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer.” Ex. 1003, Banerjee Decl. at ¶97 (citing Senzaki at 2:24-28).

It was a goal of Senzaki to produce films with mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the

deposited layer. *See* Banerjee Tr. at 102:15-13:7; Banerjee Decl. at ¶¶97; Gladfelter 2d. Decl. at ¶155. In the formation of a gate dielectric or insulator such as in a MOSFET, “typically you want a high silicon content close to the silicon substrate interface from a device point of view. And reduce the silicon content and increase [the metal] content as you move further away from the interface.” *See* Banerjee Tr. at 104:22-20. The way Senzaki achieves this, in its described “present invention,” is by changing the temperature during deposition of the gate dielectric layers. *See* Banerjee Tr. at 104:22-20. More specifically, Senzaki discloses a five-step process to produce film with mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer. *See* Senzaki at Abstract, 2:33-57; Gladfelter 2d. Decl. at ¶156; Banerjee Tr. at 109:15-110:19.

Senzaki discloses:

A process for deposition of a multiple metal and metalloid compound layer with a compositional gradient of the metal and metalloid in the layer on a substrate of an electronic material, comprising:

a) providing two or more metal-ligand and metalloid-ligand complex precursors, which preferably constitute a liquid at ambient conditions, wherein the ligands are preferably the same and are preferably selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls,

- carbonyls, pyrazoles, and their fluorine, oxygen and nitrogen substituted analogs;
- b) delivering the mixture to a deposition zone where the substrate is located;
 - c) contacting the substrate under deposition conditions with the precursors, where the contacting the substrate under deposition conditions is preferably selected from the group consisting of chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition;
 - d) varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40° C[] from said first temperature during the contact, and
 - e) depositing a multiple metal and metalloid compound layer on the substrate from the precursors resulting in the compositional gradient of the metal and metalloid in the layer as a result of step d).

Senzaki at 2:33-57 (emphasis added).

“[T]he overarching goal [of Senzaki] is to achieve a gate insulator, gate dielectric where you can control the relative ratios of silicon-containing species versus in this case the transition metal-containing species. And that’s governed by device requirements. And the way [Senzaki] achieved that as described in Senzaki is by adjusting the deposition temperature.” Banerjee Tr. at 115:7-17.

Senzaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions.” Senzaki at 3:63-4; Gladfelter 2d.

Decl. at ¶158. The “[a]ppropriate choice of precursors, in the presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxyni-trides.” Sensaki at 3:62-66 (emphasis added).

While Sensaki identifies additional deposition techniques, it describes the “present invention,” including each of its examples, as using CVD processes. Gladfelter Decl. at ¶172; Sensaki at 3:3-6, 5:10-6:21 (Examples 1-4). Sensaki’s process uses two or more metal-ligand and metalloid-ligand complex precursors in a mixture. *See* Sensaki at Abstract, 2:33-57; 5:10-6:21 (Examples 1-4); Gladfelter 2d. Decl. at ¶159; Banerjee Tr. at 108:22-109:11 (acknowledging that Sensaki’s Example 1 uses premixed mixtures of precursors). Sensaki describes that in its “present invention a new metal and metalloid deposition resulting in a compositional gradient is disclosed that can be used for precursor dispersing delivery methods, including direct liquid injection (DLI) in CVD applications.” Sensaki at 3:3-6 (emphasis added); Gladfelter Decl. at ¶172. Sensaki identifies that DLI in CVD processing “is preferred for the consistent delivery of multi-components because it delivers the same ratio of the constituents in the reactor as in the source container. DLI has the added advantage of storing precursor at room temperature and heating only the amount required for delivery, therefore improving precursor shelf life. So you keep the main part of the reactants at the ambient temperature, you don’t heat that up. And thereby you minimize the

thermal decomposition and thereby improve the shelf life of the reactor.” Banerjee Tr. at 112:11-113:18.

B. Jae-Sik Min, et al., Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethlamino)-Titanium and Ammonia (“Min”)

Min is directed to the investigation of atomic layer deposition (ALD) of amorphous TiN films on SiO₂ using the reactant sources tetrakis(ethylmethlamino)titanium (Ti[N(C₂H₅)(CH₃)₂]₄ aka “TEMAT”) and ammonia (NH₃). *See* Min at Abstract; Gladfelter Decl. at ¶61. Min found that TiN films could be formed on SiO₂ using ALD with the reactants TEMAT and NH₃, as long as the ALD process was maintained within a specific temperature range. Min at Abstract, 8; Gladfelter Decl. at ¶61. Specifically, Min found that TiN ALD required a definite temperature range between 170°C and 210°C. Min at 8; Gladfelter Decl. at ¶61. The definite temperature range is required to prevent TEMAT from decomposing thermally so that a monolayer can be chemisorbed on the surfaces. *See* Min at 8; Gladfelter Decl. at ¶61.

C. Korean Patent KR0156980 “Compound for the Deposition of Metal Nitride Thin Film and Deposition Method Thereof” (“Shin”)

Shin is directed to certain alkylamino compounds used to deposit metal nitride thin films. Gladfelter Decl. at ¶164; *see also* Shin at 1. Specifically, Shin is directed to forming titanium nitride (TiN) films using a CVD process. Gladfelter

Decl.at ¶164; *see also* Shin at 6. Shin contains no mention of an ALD process.

Gladfelter Decl.at ¶164; *see also generally* Shin. Further, Shin was disclosed during the examination process of the '016 Patent and is listed on the face of the '016 Patent. Gladfelter Decl.at ¶164; *see also* Ex. 1001.

V. PETITIONER FAILS TO ESTABLISH THAT THE INSTITUTED CLAIMS ARE OBVIOUS OVER SENZAKI IN VIEW OF MIN

Petitioner alleges that claims 1, 2, 7, and 10 are obvious over Senzaki in view of Min. Petition at 4. The Petitioner, however, has failed to prove that Senzaki in combination with Min renders obvious any of these claims.

A. The Petition Fails to Meet Its Burden to Demonstrate That Senzaki in View of Min Renders Obvious Claims 1, 2, 7, and 10

Petitioner has the burden of proof to establish that it is entitled to its requested relief. 37 C.F.R. § 42.20(c). Petitioner has the burden of proving unpatentability of claims 1, 2, 7 and 10 of the '016 Patent by a preponderance of the evidence. *See* 35 U.S.C. §316(e).

The Supreme Court in *KSR Int'l Co. v. Teleflex Inc.*, explained that, “because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known,” “it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to

combine the elements in the way the claimed new invention does.” 550 U.S. 398, 418-19 (2007).

It is not enough for Petitioner to show that a POSA, when presented with two references, would have understood that they *could* be combined. What is required is a showing that a person of ordinary skill would be motivated to pick out those two references from the universe of prior art and further pick out the specific elements required to meet the inventions claimed. *PersonalWeb Techs. LLC v. Apple Inc.*, 2017 U.S. App. LEXIS 2544, at * 14 (Fed. Cir. Feb. 14, 2017) (citing *Belden Inc. v. Berk-Tek LLC*, 805 F.3d 1064, 1073 (Fed. Cir. 2015) (“[O]bviousness concerns whether a skilled artisan not only *could have made* but *would have been motivated to make* the combinations or modifications of prior art to arrive at the claimed invention.” (emphasis original)); *InTouch Techs., Inc. v. VGO Commc’ns, Inc.*, 751 F.3d 1327, 1352 (Fed. Cir. 2014)).

Here, Petitioner relies on conclusory, self-serving statements to argue that a person of ordinary skill would have been motivated to combine Senzaki and Min. Such statements are insufficient as a matter of law and, further, are contradicted by the teachings of Senzaki and Min. Petitioner argues that a POSA would have been motivated to change the cited CVD process described in the examples of Senzaki to an ALD process to control film thickness. Petition at 38-39. But Senzaki teaches varying the temperature of deposition from a first temperature to a second

distinct temperature to achieve a compositional gradient in the resulting film through a CVD process. Sensaki at Abstract, 2:33-57, 3:40-46; 5:10-6:21, 6:27-34; *see also* Gladfelter Decl. at ¶¶182-186. Further, Sensaki teaches that varying deposition temperatures of its precursor mixtures results in varying deposition rates. Sensaki at 5:10-6:21. In other words, Sensaki teaches a complete invention, which results in oxide films having desired properties. Gladfelter Decl. at ¶182-186. Accordingly, Petitioner's argument boils down to a statement that a person of ordinary skill would reject the explicit thickness-control teachings of Sensaki in favor of an entirely different process. Gladfelter Decl. at ¶186. This argument impermissibly relies on hindsight, using the '016 Patent as an instruction manual to piece together the teachings of the prior art. *In re Fritch*, 972 F.2d 1260, 1266 (Fed. Cir. 1992).

Even if Petitioner were correct, which it is not, that a POSA would be motivated to reject the CVD teachings of Sensaki, such a person would further need to substitute the precursors used for ALD to form a nitride film taught by Min for precursor that is appropriate to form a metal oxide film by ALD. Petition at 37-42. Petitioner has made no showing that there is a reasonable likelihood of success in doing so. *See generally* Petition at 40-41; Gladfelter Decl. at ¶197-208. Further, those of ordinary skill in the art would have understood that precursors that are suitable for a CVD process cannot necessarily be assumed to work for an

ALD process. Gladfelter Decl. at ¶188. By nature, chemistry is an unpredictable, experimental science, meaning that one cannot predict the outcome of an experiment without actually carrying out the experiment. *See, e.g.*, Gladfelter Decl. at ¶188, 194, and 210; *see also Boston Scientific*, 679 F. Supp.2d at 557 (noting that “the chemical arts have long been acknowledged to be unpredictable”); *In re Carleton*, 599 F.2d at 1026 (“Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting precisely how a given compound will behave.”); *Schering Corp.*, 153 F.2d at 433 (“[O]rganic chemistry is essentially an experimental science and results are often uncertain, unpredictable and unexpected.”). Thus, modifying the example CVD process and precursors of Senzaki in view of the ALD process of Min would, at the least, require undue experimentation and therefore cannot render obvious the challenged claims of the ’016 Patent.

B. Objective Indicia Show That The Challenged Claims Are Not Obvious

As shown above, the Challenged Claims are not obvious. Petitioner has not met its burden to establish a *prima facie* case, much less a strong one. The question of obviousness must be resolved on the basis of the factual inquiries including objective evidence if presented. In fact, the Federal Circuit has

explained the importance of secondary considerations in “guard[ing] as a check against hindsight bias.” *In re Cyclobenzaprine Hydrochloride Extended-Release Capsule Patent Litig.*, 676 F.3d 1063, 1079 (Fed. Cir. 2012).

As discussed above, the inventions are in an unpredictable, experimental field, meaning that even one skilled in the art cannot predict the outcome of an experiment regarding a class of precursors without actually performing it or a substantially similar one in a laboratory. Once the inventors tested the claimed methods and the class of compounds in the laboratory, they found that they possessed unexpectedly advantageous and superior properties, including liquid state at room temperature, higher decomposition temperature, higher volatility, and other surprising results as reported by the inventors in the patent specification and elsewhere. Ex. 1001 at 19:31-48 (“surprisingly efficient,” “surprisingly fast,” and “surprisingly” successful at providing films over very high aspect ratios); *see also* Ex. 2137, Hausmann. Further, the use of the metal alkylamide precursors claimed in the challenged claims resulted in the deposition of metal oxide at unprecedented low temperatures and with the unexpected lack of detectable impurities such as carbon. *See, e.g.*, Ex. 1001 at 26:65-66; *see also* Ex. 2137. These unexpected properties and results cannot be ignored. In addition to the demonstration of such unexpectedly superior properties, the intrinsic record demonstrates that the inventions solved a long-felt need of the industry and have since achieved great

commercial success. During the prosecution of the '848 Patent, from which the '016 Patent is a direct continuation, the patentee established the long-felt need and failure of others. *See*, Ex. 1014, ("Gordon Aug. 2008 Decl."). The need to solve the problem of deposition of high dielectric materials inside narrow trenches for DRAM memory existed as early as the mid-1990s and was recognized by those of ordinary skill in the art. In fact, industry experts working on the 2000 International Technology Roadmap for Semiconductors did not expect a solution to this problem until *at least* 2008. Ex. 2108, ITRS. In the 1990s, there was a high degree of interest in investigating precursors for ALD. For example, a joint scientific paper written by Samsung Electronics and Genus Inc. (an ALD equipment supplier) confirms this point. *See* Ex. 2136, Lee. Samsung and Genus had many highly-skilled scientists and technologists working on, and failing to solve, the very problems that Petitioner now claims were only the ordinary development of technology. Despite such active efforts, this problem was not solved before the current invention was made by Dr. Gordon et al. In fact, the Samsung Paper specifically thanked Dr. Gordon for his teaching of the claimed inventions. *See* Ex. 2136 at 2 ("The authors would like to thank Professor R. Gordon, D. Hausmann at Harvard University for helpful discussions on alkylamide precursors.")

As shown above, Petitioner has failed to meet its burden of even a *prima facie* case of obviousness. However, even if it had, the establishment of a *prima facie* case is not a conclusion on the ultimate issue of obviousness. Evidence arising out of secondary considerations must always be considered, at least in part because, as the Federal Circuit has noted, it “is an important component of the obviousness inquiry because ‘evidence of secondary considerations may often be the most probative and cogent evidence in the record. It may often establish that an invention appearing to have been obvious in light of the prior art was not.’” *Transocean Offshore Deepwater Drilling, Inc. v. Maersk Drilling USA, Inc.*, 699 F.3d 1340, 1349 (Fed. Cir. 2012) (quoting *Stratoflex, Inc. v. Aeroquip Corp.*, 713 F.2d 1530, 1538 (Fed. Cir. 1983)).

C. Independent Claim 1 Is Not Obvious Over Senzaki in view of Min

A POSA would not have combined Senzaki and Min to arrive at the subject matter of claims 1, 2, 7, or 10. Gladfelter Decl. at ¶¶ 178-214.

As the Board recognizes “Senzaki does not disclose an explicit example of forming a metal oxide layer using a metal alkylamide in an ALD process.”

Institution Decision at 10; Gladfelter 2d. Decl. at ¶160. Petitioner, however, alleges that Senzaki discloses that its processes can be implemented using ALD and that a POSA would have implemented Senzaki’s Example 1, which uses a metal alkylamide, using ALD. *See, e.g.*, Petition at 34 (citing Senzaki at 3:40-44

(referring to Example 1), 4:4-15, 5:11-42 (Example 1)). However, a POSA would not have understood Senzaki as disclosing an ALD process using a metal alkylamide precursor.

Additionally, as the Petitioner recognizes, the deposition process required by claims 1, 2, 7, and 10 is a self-limiting ALD process with a specific type of precursor to form a specific type of insulator film. Gladfelter Decl. at ¶180; Petition at 29. “Petitioner concedes that Senzaki does not explicitly state that the depositions of the first precursor and the second reactant are self-limiting.” Institution Decision at 9 (citing Petition at 31-35). In an attempt to cure the deficiencies with Senzaki, Petitioner argues that one of ordinary skill would modify Senzaki’s process in view of Min. *See* Gladfelter Decl. at ¶181; Petition at 37. However, as discussed in more detail below, a POSA would not have combined the teachings of Senzaki and Min to arrive at a self-limiting ALD process using a metal alkylamide precursor to deposit a metal oxide film. *See* Gladfelter Decl. at ¶¶178-214.

1. Senzaki Does Not Disclose Which, If Any, Of Its Precursors Are Suitable For Use in an ALD Process

Petitioner asserts, in its description of Senzaki, that Senzaki states that the film formed by CVD in Example 1 could also be formed by ALD. Petition at 24 (citing Senzaki at 4:4-9). The Board also relies on this passage of Senzaki to

conclude that “Senzaki explains that the disclosed precursors could also be deposited by atomic layer deposition.” Institution Decision at 6 (citing Senzaki at 5:50, 4:4-9). However, a POSA would not consider Senzaki as providing a blanket disclosure that its precursors could also be deposited by ALD. Gladfelter 2d. Decl. at ¶164; Gladfelter Decl. at ¶176. In fact, Petitioner’s expert, Dr. Banerjee, identified that to determine whether one of Senzaki’s precursors could be used in ALD, a POSA would need to first look at information in available references and then “of course, at the end of the day, [a POSA] would have to do some experimentation.” Banerjee Tr. at 117:18-118:4, 142.

As discussed above, a POSA would understand that the precursor chemistry involved in the formation of a metal film via an ALD process is unpredictable. Gladfelter Decl. at ¶110. Accordingly, a POSA would not understand Senzaki’s identification that techniques other than CVD, such as ALD, may be used as identifying that these techniques are suitable for use with each disclosed precursor. Gladfelter 2d. Decl. at ¶165; Senzaki at 2:44-50; 4:4-15 (identifying low pressure CVD, atmospheric pressure CVD, sub-atmospheric pressure CVD, plasma, photo, radical, or laser enhanced CVD deposition, and jet vapor deposition well recognized deposition techniques, and atomic layer deposition as potentially suitable techniques for the disclosed process). Rather, a POSA would understand, as Senzaki specifically provides, that the “[a]ppropriate choice of precursors, in the

presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxynitrides.” Sensaki at 3:62-66 (emphasis added).

Senzaki does not state that its precursors, including those used in its Example 1, can be used for both CVD and ALD, but rather asserts that techniques other than CVD, such as ALD, may be used, provided that there is an “[a]ppropriate choice of precursors” and deposition conditions. Gladfelter 2d. Decl. at ¶166; Gladfelter Decl. at ¶176; Sensaki at 3:63-4:9. Sensaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions.” Sensaki at 3:63-4; Gladfelter 2d. Decl. at ¶166. However, Sensaki does not identify the proper precursors or conditions necessary for an ALD process. Gladfelter 2d. Decl. at ¶166; Gladfelter Decl. at ¶176; Sensaki at 3:63-4:9. For example, as the Board acknowledges, while Sensaki describes the use of precursor source mixture metal including a metal alkylamide, $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$ and $\text{Si}[\text{N}(\text{CH}_3)_2]_4$, in a CVD process in Example 1, “Senzaki does not disclose an explicit example of forming a metal oxide layer using a metal alkylamide in an ALD process.” *See* Institution Decision at 10. In fact, Sensaki does not disclose a single example of an ALD process or identify a single precursor that would be suitable for an ALD process. Gladfelter 2d. Decl. at ¶167.

In describing its precursors, Senzaki identifies that the metalloid is preferably silicon, but may be boron, silicon, arsenic, tellurium, or mixtures thereof. Senzaki at 4:60-62. “The metal is selected from any metal of the Periodic Table of the Elements” (*Id.* at 4:63-64 (emphasis added)) and is preferably,

zinc, cadmium, mercury, aluminum, germanium, gallium, indium, thallium, tin, lead, antimony, bismuth, lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, cerium and mixtures thereof.

Senzaki at 4:63-5:7. The ligands may be from any one of fourteen (14) classes of ligands, selected from the group consisting of

alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, β diketonates β ketoiminates, β diiminates, pyrazoles and their fluorine, oxygen and nitrogen substituted analogs.

Senzaki at 3:54-61. Senzaki fails to provide any guidance regarding which metal-ligand or metalloid-ligand combinations are preferable. Gladfelter 2d. Decl. at ¶169. Further, the classes of ligands identified by Senzaki include numerous

permutations. *Id.* However, Senzaki fails to provide any guidance regarding preferred permutations. *Id.*

A POSA would have understood that not every precursor disclosed in Senzaki can be used for both CVD and ALD. Gladfelter 2d. Decl. at ¶170; *see also* Banerjee Tr. at 66:18-67:7, 74:15-23. A POSA would also understand that when designing a CVD or ALD process, one must consider the precursor and deposition conditions. *See* Gladfelter 2d. Decl. at ¶170; *see also* Banerjee Tr. at 65:11-14 (“when you talk about CVD or ALD processes, you cannot divorce the molecule from the deposition conditions.”) As Petitioner’s expert, Dr. Banerjee, testified, “[y]ou can always choose wrong deposition conditions and the process would not work.” Banerjee Tr. at 78:14-79:4.

In considering whether one of Senzaki’s precursors can be used in an ALD process, a POSA would first have to consider additional references and then second would have to test the precursor to determine its suitability. Gladfelter Decl. 2d. Decl. at ¶164; Banerjee Tr. at 117:18-4; *see also id.* at 73:15-74:14; 96:9-97:6. When questioned how a POSA would know if Senzaki’s precursors were suitable for ALD, Petitioner’s expert, Dr. Banerjee, testified that “what one would do is look at information that is readily available in handbooks or on the Internet to guide your choice and use thermodynamics as the initial guide. But of course, at

the end of the day, you would have to do some experimentation.” Banerjee Tr. at 117:18-118:4, 142 (emphasis added).

Senzaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions,” but fails to disclose any particular precursor as suitable for ALD or disclose the set of ALD conditions necessary to run a successful ALD process. Gladfelter 2d. Decl. at ¶170; Senzaki at 3:63-4.

2. A POSA Would Not Have Found It Obvious To Implement Senzaki’s Process Using ALD

Petitioner alleges that Senzaki discloses an ALD process using a metal alkylamide precursor. *See* Petition at 34. Particularly, Petitioner relies on Senzaki’s disclosure that its process is not specifically limited to CVD and Senzaki’s disclosed CVD process using a metal alkylamide precursor in Example 1, to assert that such a process could be implemented using ALD. *See, e.g.*, Petition at 34 (citing Senzaki at 3:40-44 (referring to Example 1), 4:4-15, 5:11-42 (Example 1)); *see also* Petition at 32-22 (“Senzaki states that its processes can be performed using ALD”) (citing Senzaki at 4:4-15). However, a POSA would not have understood Senzaki as disclosing or rendering obvious an ALD process using a metal alkylamide precursor. Gladfelter 2d. Decl. at ¶171.

As Petitioner’s expert, Dr. Banerjee, recognizes, Senzaki’s process requires the formation of a metal and metalloid compound layer with a compositional

gradient of the metal and metalloid in the layer. Banerjee Tr. at 102:3-14; *see also* Senzaki at Abstract, 2:33-57, 3:40-46, 6:27-34; Gladfelter Decl. at ¶83, 171. To achieve this, Senzaki describes that its process varies the temperature of deposition from a first temperature to a second distinct temperature. *See* Senzaki at Abstract, 2:33-57, 3:40-46, 6:27-34; Gladfelter Decl. at ¶83, 171; Banerjee Tr. at 102:3-14, 108:6-9; Institution Decision at 6.

Example 1 in Senzaki describes a CVD process using a $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$ and $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ mixture to form a metal/metalloid film with a compositional gradient. Senzaki at 5:10-42. In an attempt to describe how Senzaki's Example 1 could use an ALD process rather than a CVD process, Petitioner's expert, Dr. Banerjee, asserts that in order to achieve a compositional gradient, one would "tweak[]" the ratio of the silicon and zirconium during the ALD process. *See* Banerjee Tr. 105:14-106:5. More of the $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ than the $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$ would be allowed to flow in the initial stages. *See id.* "But then as you build up the layers towards the latter part of the process, [] you change the temperature and you'd change the ratio of the zirconium containing flux versus the silicon containing flux. You have more of the zirconium-containing precursor flowing to the reactor and less of the silicon-containing precursor." *See* Banerjee Tr. 105:14-106:5. Dr. Banerjee testified that for the ALD process, a POSA would choose a deposition temperature within the ALD window of both the metal,

Zr[N(CH₂CH₃)₂]₄, and metalloid, Si[N(CH₃)₂]₄, precursors used. *See* Banerjee Tr. at 110:25-111:22.

A POSA considering Senzaki would not have found it obvious to implement such an ALD process. Gladfelter 2d. Decl. at 174. Senzaki provides no disclosure of varying the ratio of precursors inserted into the deposition chamber during the process. *Id.* In fact, Senzaki discloses that the precursors are premixed before the deposition process begins. *Id.*; Banerjee Tr. at 108:22-109:11 (acknowledging that Senzaki's Example 1 uses premixed mixtures of precursors). Premixing the precursors would prevent the ability to vary the ratio of precursors during deposition. Gladfelter 2d. Decl. at ¶174. Dr. Banerjee alleges that the precursors could be kept separate, however, such a disclosure is not present in Senzaki. *See* Banerjee Tr. at 108:22-109:11; Gladfelter 2d. Decl. at ¶174.

Additionally, Senzaki provides no discussion of the process conditions necessary to run an ALD process or whether precursors will have overlapping ALD windows. Gladfelter 2d. Decl. at ¶175. The specification includes the following statement for choosing an appropriate mixture of precursors.

The volatile components are chosen such that:

- 1) They are chemically compatible, therefore, no nonvolatile polymeric or multinuclear species are formed.

- 2) No precipitates are generated due to ligand exchange on the metals or inter ligand reactions.
- 3) The mixtures maintain low viscosity and thermal stability.
- 4) Undesired redox chemistry will not take place (eg. $M+1 + M'+3 \rightarrow M+2 + M'+2$).

Senzaki at 3:6-17. A POSA would recognize that Senzaki does not teach that the precursor mixture (or even the individual components of the precursor mixture) must be capable of self-limited deposition as required in ALD. Gladfelter 2d. Decl. at ¶175.

Further, a POSA would understand that different ALD precursors can have different ALD windows. Gladfelter 2d. Decl. at ¶176.

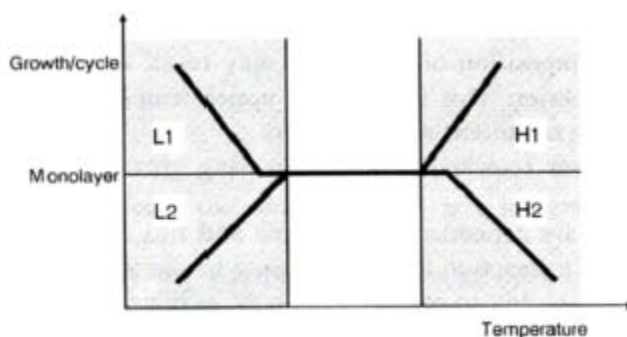


Fig. 12. A processing window of the ALE process. A full monolayer saturation $f_s = 1$ for both reactants is assumed. Limiting mechanisms in the different areas of the chart are: (L1) condensation of a reactant occurs; (L2) activation energy of a necessary reaction is not exceeded; (H1) decomposition of a reactant results in a non-evaporating surface layer on a monolayer; (H2) re-evaporation of a formed monolayer occurs.

Ex. 2123, Suntola III at 23 (Figure 12). The above figure illustrates the effect of temperature on ALD processes where the optimum temperature region is referred to as the ALD window. See Gladfelter 2d. Decl. at ¶¶176; 75. The ALD window

is the temperature region where the growth per ALD cycle is constant as a function of temperature. *Id.* at ¶176; 75. For a given ALD precursor, the temperatures corresponding to the beginning and end of the ALD window depend on the physical properties and chemical reactivity (including thermal stability) of the precursor. *Id.* at ¶75. Consequently, this flat region, where growth per ALD cycle is constant as a function of temperature, enables consistent growth of single layer films over high aspect-ratio surfaces. *Id.* In the region designated H1 in the above figure, the growth per cycle increases with increasing temperature. *Id.* at ¶80. At a sufficiently high temperature the activation energy of the thermal decomposition of the precursor complex is exceeded, resulting in the uncontrolled thermal decomposition of the precursor complex. *Id.* In region H1, the film growth transitions to a CVD process resulting in continuous deposition onto the surface. Gladfelter 2d. Decl. at ¶80; *see* Banerjee Tr. at 128:2-129:4.

Petitioner's expert, Dr. Banerjee, acknowledges that ALD is self-limiting within the ALD window and asserts that a POSA would choose a common window between the metal and metalloid precursors used. Banerjee Tr. at 29:3-17, 111:6-19. However, Senzaki makes no mention of temperature windows or what precursors could be used together in an ALD process. Gladfelter 2d. Decl. at ¶177. When asked whether the precursors used in Senzaki's Example 1 has a common

window, Banerjee identified that he did not know. *See* Banerjee Tr. at 110:25-111:22.

A POSA would understand that precursors fulfilling the four requirements listed by Senzaki may not be suitable for ALD and do not have ALD windows, let alone ALD windows that overlap with the other precursors in a mixture. *See* Gladfelter 2d. Decl. at ¶178-179 (proving an example precursors that do not have overlapping ALD windows); Senzaki at 3:6-17. This means that there would be no temperature at which both precursors simultaneously exhibit self-limiting, ALD behavior. *See* Gladfelter 2d. Decl. at ¶178.

Petitioner's expert, Dr. Banerjee, also ignores potential problems with the simultaneous injection of two precursors. Gladfelter 2d. Decl. at ¶180. In ALD, simultaneous injection of two precursors would require them to compete for the same surface sites. *Id.* If one precursor reacts more rapidly with the surface sites, it is possible that it will saturate or all of the surface sites before the second precursor has a chance to react. *Id.* As a result, the composition of the film will depend upon more than just varying the ratio of the precursors introduced into the system. *Id.*

Senzaki does not address the numerous issues faced with designing an ALD process. Gladfelter 2d. Decl. at ¶181. As a result, while a POSA may not consider Senzaki to be limited to a CVD process, a POSA would not understand Senzaki to

disclose or render obvious any particular ALD process, let alone an ALD process as recited by Claim 16 of the '016 Patent. *Id.*

**3. A POSA Would not have been Motivated to Combine
Senzaki and Min to Arrive at the Process Recited by Claim
1 of the '016 Patent**

**a. A POSA would understand that Senzaki and Min
have directly contrary goals**

The Petitioner argues that a person of ordinary skill would have been motivated to combine Senzaki and Min because both references teach the same goals of precisely controlling the film thickness. Petition at 38-39. Specifically, the Petitioner argues that a POSA “would have been motivated to implement Min’s self-limiting teachings to achieve the goals of Senzaki and precisely control the thickness” of an insulator. *Id.* at 39. The Petitioner ignores the express goals of Senzaki and Min which are completely contrary to each other. Gladfelter Decl. at ¶182. Particularly, Senzaki seeks to deposit a film with a compositional gradient by varying the temperature of the deposition process. Gladfelter Decl. at ¶183; Senzaki at Abstract, 2:33-57, 3:40-46, 6:27-34. Min, on the other hand, seeks to find a stable temperature within an ALD window, to deposit a nitride film through a self-limiting ALD process. Min at Abstract, 8; Gladfelter Decl. at ¶61.

A POSA would understand that Senzaki discloses the express goal of varying the temperature of deposition from a first temperature to a second distinct

temperature to achieve a compositional gradient in the resulting film. Gladfelter Decl. at ¶183; Senzaki at Abstract, 2:33-57, 3:40-46, 6:27-34. Petitioner's expert, Dr. Banerjee, testified that "the overarching goal [of Senzaki] is to achieve a gate insulator, gate dielectric where you can control the relative ratios of silicon-containing species versus in this case the transition metal-containing species. And that's governed by device requirements. And the way [Senzaki] achieved that as described in Senzaki is by adjusting the deposition temperature." Banerjee Tr. at 115:7-17 (emphasis added).

Varying the temperature to achieve a compositional gradient is central to the teachings of Senzaki, and a POSA would have understood that Senzaki's teachings regarding the temperature change are not limited to the CVD examples disclosed in Senzaki. Gladfelter 2d. Decl. at ¶184. As the Board acknowledges, "[i]n the process of Senzaki, . . . [t]he temperature of the deposition is [] varied by at least 40° C to deposit a metal/metalloid compound layer have a compositional gradient." Institution Decision at 6. Senzaki specifically identifies that its process requires "varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40° C[] from said first temperature during the contact." Senzaki at 2:33-57, Abstract. This is further acknowledged by Petitioner's expert, Dr. Banerjee. Banerjee Tr. at 108:6-9 (confirming that "Senzaki teaches varying the composition by varying the deposition temperature.")

In fact, Senzaki's process is designed to specifically "address[] the purported failure of the prior art to provide a desirable method for controllably producing a mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer." Banerjee Decl. at ¶97 (citing Senzaki at 2:24-28). The way Senzaki achieves this, in its described "present invention," is by changing the temperature during deposition of the gate dielectric layers. *See* Banerjee Tr. at 104:22-20.

A POSA would understand that Senzaki specifically identifies that its process requires "varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40° C. from said first temperature" for any of its referenced deposition processes, "chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition." Gladfelter 2d. Decl. at ¶185; Senzaki at 2:33-60. Senzaki states that it is "preferable" to vary the temperature during deposition in a constant manner from the low starting temperature to the high ending temperature. Senzaki at 4:25-28. Each of the examples in Senzaki purposely varies the deposition temperatures. *See* Senzaki at 5:10-6:21 (Examples 1-4) ("between 280 and 430°C"; "between 300 and 360°C"; "between 300 and 435°C"; and "between 310 and 350°C").

Min, however, is directed to an ALD process run at a particular temperature within an ALD window in order to achieve self-limiting deposition. Gladfelter 2d. Decl. at ¶186; Petition at 26, 38. As Petitioner indicates, Min teaches as a goal self-limiting deposition as a distinct characteristic of an ALD process. Petition at 38; *see also* Min at 9. Min teaches, and a POSA would understand, that in Min's self-limiting deposition, "film thickness per cycle is independent of substrate temperature." Gladfelter Decl. at ¶185; Min at 8. This is achieved by maintaining the deposition temperature within an "ALD window." Gladfelter 2d. Decl. at ¶186.

It is common for ALD processes to exhibit an "ALD window" in temperature, where the growth rate of the process is constant due to the saturation and self-limiting behaviour of the chemical species at the surface. Gladfelter Decl. at ¶186; Banerjee Tr. at 29:3-6 ("So by ALE or ALD window, you're talking about choosing substrate temperatures and a dose where the growth may be self limiting"). In fact, Fig. 3 of Min depicts such an ALD window in which the deposition rates is independent of deposition temperature. Min at Fig 3, 8 (in case of (a), film thickness per cycle is independent of substrate temperature between 170°C and 210°C.)

As a result, a POSA would understand that the goals of Senzaki are at odds with those of Min. Gladfelter Decl. at ¶186. First, a POSA would recognize that

Senzaki's goal of achieving a compositional gradient by varying the deposition temperature is directly at odds with Min's goal of running an ALD process at a specific temperature within an ALD window to achieve self-limiting deposition. Second, a POSA would recognize that if Senzaki's process were configured to operate at a single temperature or within an ALD window disclosed by Min, the deposited film would not include Senzaki's desired compositional gradient. Gladfelter 2d. Decl. at ¶188; Gladfelter Decl. at ¶186.

As discussed above in Section V.C.2, Petitioner's expert, Dr. Banerjee, proposes modifying Senzaki's process to use ALD by choosing a deposition temperature within the ALD window of both the metal and metalloid precursors and achieving a compositional ratio by manually controlling the flow ratio of the individual precursors. *See* Banerjee Tr. at 105:14-106:5, 110:25-111:22. However this type of process is not disclosed by either Senzaki or Min. Gladfelter 2d. at ¶189. Further, Dr. Banerjee's proposed ALD process includes changing the temperature during the deposition process as the ratio of the precursors is changed. *See* Banerjee Tr. at 105:14-106:5; Gladfelter 2d. Decl. at ¶189. A POSA would recognize that Min provides no disclosure regarding an ALD process with changing deposition temperatures. And further, if the process temperatures were allowed to vary outside of the ALD window, the process would not be controlled

self-limiting ALD as desired by Min. Gladfelter 2d. Decl. at ¶189; Gladfelter Decl. at ¶186.

b. A POSA would not have understood modifying Senzaki's CVD process in view of Min to yield predictable results nor be routine to implement

The Petitioner argues that a person of ordinary skill would have understood that modifying Senzaki with Min would “yield predictable results and would have been routine to implement.” Petition at 39. Particularly, the Petitioner points to Senzaki's CVD example processes utilizing precursor mixtures containing a metal alkylamide and argues that a POSA would be motivated to modify them based on Min's teachings. *Id.* at 40, *see also* Senzaki at 5:11-58 (Examples 1, 2). Petitioner, however, ignores the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD. Gladfelter Decl. at ¶187.

First, a POSA would not have modified the cited Senzaki CVD processes in view of Min due to the unpredictable nature of ALD and CVD processes. *See* Section II.B.1II.B.1, above; Gladfelter Decl. at ¶188, 119-121. A POSA would have known that a CVD process cannot be predictably adapted to ALD. *See* Section II.B.1, above (providing example CVD processes that cannot be modified to ALD); Gladfelter Decl. at ¶119-121, 188(same). Min itself found that films deposited by CVD were different than those deposited by ALD. Gladfelter Decl. at ¶188; *see also* Min at 8. Additionally, as discussed above, a POSA would have

known that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD. Gladfelter Decl. at ¶188; Banerjee Tr. at 66:18-67:7 (“Yes, there can be some where CVD precursors may not work for ALD, that's correct.”), 74:15-23 (“Not all CVD precursors may work for ALD. . .”). As explained by Dr. Gladfelter, a POSA would not even know a priori (before experimentation) that a precursor would have an “ALD window” where deposition is self-limiting. Gladfelter Decl. at ¶¶184-86.

Further, the detailed description of Senzaki makes a single reference to ALD in a single paragraph consisting of eight lines of text, but fails to provide any specifics regarding how an ALD process would be implemented with the precursor mixtures or how ALD could be used to achieve a compositional gradient. Senzaki at 4:8-15; Gladfelter Decl. at ¶189; *see also* Sections V.C.1, V.C.2.

Second, a POSA would not have modified the cited Senzaki CVD processes in view of Min because Min discloses a highly specific ALD process and provides limited teachings. Gladfelter Decl. at ¶190. A POSA considering Senzaki in view of Min would have had no reasonable expectation that the cited Senzaki CVD processes could be successfully modified based on Min’s specific ALD process. *Id.*

A POSA would have recognized that Min is directed to the specific investigation of ALD using TEMAT and NH_3 to produce TiN films on SiO_2 . Gladfelter Decl. at ¶91; Min at Abstract. A POSA would have known that Min's specific teachings are not transferrable to all ALD processes. Gladfelter Decl. at ¶191. For example, Min identifies that its ALD process is not typical of other ALD processes because it deposited films with a thickness of 1.6ML/cycle. *See* Min at 10; Gladfelter Decl. at ¶191.

A POSA would recognize that Min provides no teachings with respect to the use of other reactants, such as oxygen or water, with metal alkylamides. Gladfelter Decl. at ¶192. Further, Min provides no teaching with respect to the deposition of films other than nitride films, such as oxides. *Id.* A POSA would have no reasonable expectation based on Min's teachings that an ALD process using metal alkylamides with oxygen would successfully result in the deposition of a metal oxide film. *See* Section II.B, above; Gladfelter Decl. at ¶192, 119-121

Thus, a POSA would not have expected that modifying the cited CVD deposition examples in Senzaki in view of Min would yield predictable results or would have been routine to implement as a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD. *See* Gladfelter Decl. at ¶193.

c. A POSA would not have known that certain precursors were “desirable” for ALD processes

Petitioner argues that the precursors disclosed in Senzaki and Min “possess such characteristics as stability, volatility, and reactivity” and further that “[t]hese characteristics were known to be desirable in ALD precursors for self-limiting processes.” Petition at 40. Petitioner’s argument ignores the state of the art at the time of Senzaki, Min and the ’016 Patent. *See* Section II.B, above; Gladfelter Decl. at ¶194. A POSA would have understood that it was not possible to ascertain whether a precursor could be successfully used in an ALD process to form a metal oxide film without extensive experimentation. *Id.* A POSA would have understood that volatility, thermal stability, and high reactivity are useful characteristics for precursors in both CVD and ALD. Gladfelter Decl. at ¶194. However, the fact that a precursor exhibited these characteristics would not provide a reasonable expectation that the precursor could have been successfully employed in a CVD or an ALD process. *See* Section II.B, above; Gladfelter Decl. at ¶194.

As stated before and as will be detailed further below, in this context it is inaccurate to state that metal alkylamides were known to be desirable for forming metal oxide films via self-limiting ALD. Gladfelter Decl. at ¶195. This was not known at the time of the inventions. The Examiner correctly stated that the prior

art, including the 1999 Min reference, taught the use of a metal alkylamide to form a titanium-silicon-nitride film by ALD, but did not teach or suggest forming a metal oxide by ALD using metal alkylamides. Ex. 1002 at 24.

Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting with a reasonable degree of confidence how a given compound will behave. *See* Section II.B, above; Gladfelter Decl. at ¶196.

d. A POSA would have had no reasonable expectation of success modifying Senzaki's CVD process in view of Min

The Petitioner argues that given Min's teaching, a POSA would have had a reasonable expectation of success in modifying the cited Senzaki CVD processes with Min's self-limiting ALD process. Petition at 40-41. In particular, the Petitioner argues that "[o]ne of ordinary skill in the art would not have been deterred by the fact that Min describes formation of a metal nitride film rather than an insulator such as a metal oxide." *Id.* The Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD. Gladfelter Decl. at ¶197.

Min's teachings are limited to the use of ALD for forming TiN films and one of ordinary skill would not have had a reasonable expectation that those teachings could be successfully generalized to other systems, such as that proposed

by the Petitioner. Gladfelter Decl. at ¶198. For example, the data presented in Min's FIG. 3 shows a narrow temperature window, i.e., between 170°C and 210°C, in which the TiN film growth is self-limiting (a so-called ALD window).

Gladfelter Decl. at ¶199. The ALD window depends not only on the properties of the precursor but also those of the reactant. Gladfelter Decl. at ¶199. Min indicates that TiN films "are not deposited below 150 C, indicating that reactant sources are mainly physisorbed on the surface below 150 C." Min further explains that "[c]hemisorption involves the formation of relatively strong chemical bonds whereas in physisorption, the effective forces are of weak van der Waals type. Thus, weak bonds of physisorption can be easily purged by Ar." Min at 8. Min further explains that above 230 C, the deposition process transitions from an ALD process to an MOCVD process, which is not self-limiting. *Id.*

It is not, however, possible to predict with any reasonable degree of confidence whether changing any of the precursor or the reactant of an ALD system would result in a system for which an ALD window would be available. Gladfelter Decl. at ¶200; *see also* Section II.B, above. For example, a change of the reactant may result in a system in which the chemisorption of the reactant would occur at such elevated temperatures at which the precursor would not be thermally stable. Gladfelter Decl. at ¶200. In fact, as discussed above, precursor-reactant systems are known that can be successfully used in a CVD process, but

not in an ALD process because of the lack of a suitable ALD window (e.g., Tetramethysilane, $\text{Si}(\text{CH}_3)_4$). Gladfelter Decl. at ¶200; *see also* Section II.B, above.

In the present case, a POSA would not have been able to predict with any reasonable degree of confidence whether replacing ammonia with an oxygen-containing compound, such as water, in Min's system would result in a system for which an ALD window would be available. Gladfelter Decl. at ¶201.

Further, a POSA would have understood that modifying Min's ALD process to form an oxide film, rather than a nitride film, which is the focus of Min's teachings, can pose a number of difficulties. Gladfelter Decl. at ¶202. A person of ordinary skill would understand that using a metal dialkylamide precursor to form a metal oxide involves the high possibility of the introduction of both carbon and nitrogen as impurities into the growing oxide film. Gladfelter Decl. at ¶202; *see also* Section II.B.2, above. A person of ordinary skill would further recognize that the alternate introduction of a metal dialkylamide precursor and an oxidizing agent, as in ALD, onto a substrate would likely increase that possibility. Gladfelter Decl. at ¶202. The alternate introduction of a metal dialkylamide precursor and an oxidizing agent, onto a substrate would likely result in the adsorption of at least part of the precursor on the substrate and its presence on the substrate surface by itself for a period of time prior to the introduction of the oxidizing agent. *Id.*

During such a period, carbon and nitrogen of the precursor could be incorporated into the growing film. *Id.*

In Min, nitrogen is a constituent of the TiN film. As such, in Min, the nitrogen of the dialkylamide precursor is not a potential undesired impurity. *Id.* at ¶203. In other words, in Min, only the carbon of the dialkylamide precursor would be a potential impurity in the growing film. *Id.* In contrast, if one were to use a dialkylamide precursor to form an oxide film, both nitrogen and carbon of the precursor would be potential impurities. *Id.*

Further, a POSA would have understood that Min's use of ammonia as a reactant reduces carbon impurities. Gladfelter Decl. at ¶204. Ammonia, however, is not useful when forming a metal oxide because it does not contain oxygen. *Id.* As such, one of ordinary skill would have understood that the teachings of Min regarding the formation of a TiN film is not simply transferrable to the formation of a metal oxide film. *Id.*

The Petitioner argues a POSA would not be deterred by the fact that Min only discloses the formation of nitride films because "Senzaki teaches that the same precursor may be used to form either a metal oxide or a metal nitride film." Petition at 41. Each of the portions of Senzaki cited in support of this false premise are directed to CVD examples in which the temperature of deposition is being varied to result in a compositional gradient. Gladfelter Decl. at ¶206. These

cited portions of Senzaki do not mention ALD and it is well known that the requirements of ALD precursors differ from those of CVD. Gladfelter Decl. at ¶206; *see also* Ex. 1012 at 13. Thus, any purported teachings by these sections of Senzaki are limited to CVD.

Next, both the Petitioner and Dr. Banerjee incorrectly allege that “other prior art” references confirm that metal precursors may be used to form either a nitride or oxide film. Ex. 1003, at ¶134; Petition at 41. The allegedly supporting references, however, are not directed to metal alkylamide precursors or only discuss CVD processes. Gladfelter Decl. at ¶207; *see* Ex. 1008 (providing no discussion of alkylamide precursors); Ex. 1011 (same); Ex. 1012 (same); Ex. 1013 (referring only to certain CVD processes). Therefore, as established above, they are no more helpful/motivating to a POSA than the references which have already been overcome in the prosecution of the ’016 application. *See* Ex. 1002 at 24.

As such, a POSA would have no reasonable expectation of success in modifying the Senzaki CVD processes in view of Min to obtain a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD. Gladfelter Decl. at ¶208.

e. A POSA would not have found it obvious to try modifying Senzaki's CVD process in view of Min

Petitioner argues that for the same reasons as above, it would have been obvious to a POSA to try the combination of Senzaki in view of Min. Petition at 42.

As discussed above, a POSA would understand that precursor chemistry is unpredictable and that one could not predict with any reasonable degree of confidence that the mixtures of precursors used in Senzaki could be successfully used in an ALD process to form an oxide film. *See* Section II.B, above; Gladfelter Decl. at ¶210. More generally, a POSA would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work in an ALD process due to the different requirements of CVD and ALD. *Id.*

Further, the Petitioner states that “such optimization of process conditions to achieve approximately one monolayer per ALD cycle is routine in semiconductor fabrication” and that Min teaches “advantages of monolayer deposition with self-limiting deposition conditions.” Petition at 42. However, as discussed above, one of ordinary skill in the art would have recognized that the goals of Senzaki are contrary to the alleged advantages of self-limiting deposition as taught in Min. Gladfelter Decl. at ¶211.

As stated above, a POSA would recognize that in Senzaki, varying deposition temperatures of precursor mixtures results in varying deposition rates as shown in Senzaki's examples. *See* Senzaki at 5:10-6:21; Gladfelter Decl. at ¶212.

In Min, however, the growth rate of the deposited film is independent of the deposition temperature within the ALD window. Min at 8 (right) ("film thickness per cycle is independent of substrate temperature."). This advantage and characteristic of Min is directly at odds with the goals of Senzaki. Gladfelter Decl. at ¶213.

Thus, a POSA considering the variable deposition rates and compositional gradients of Senzaki would have no motivation to look to Min's teachings regarding the deposition of metal nitride films via ALD to obtain a process for forming a metal oxide film using an alkylamide precursor in a self-limiting ALD process. Gladfelter Decl. at ¶214.

VI. PETITIONER FAILS TO ESTABLISH THAT THE INSTITUTED CLAIMS ARE OBVIOUS OVER SENZAKI IN VIEW OF MIN AND SHIN

Petitioner alleges that claim 8 is obvious over Senzaki in view of Min and Shin. Petition at 4. The Petitioner, however, has failed to prove that Senzaki in combination with Min and Shin renders obvious any of these claims.

A POSA would not have combined Senzaki in view of Min and Shin to arrive at the subject matter of Claim 8. Gladfelter Decl.at ¶216.

Petitioner admits that Senzaki and Min do not disclose the subject matter of Claim 8. Petition at 45. Specifically, Petitioner indicates that Senzaki and Min do not disclose tetrakis(ethylmethyamido)zirconium. *Id.* As described above, a POSA would not be motivated to attempt to combine Senzaki and Min to achieve a process to form a metal oxide film using an alkylamide precursor in a self-limiting ALD process. Gladfelter Decl.at ¶217. In addition, a POSA would not have a reasonable expectation of success in an attempt to combine Senzaki and Min to achieve a process to form a metal oxide film using an alkylamide precursor in a self-limiting ALD process. *Id.* Shin does not provide this motivation or expectation of success, nor does the Petitioner assert that it does. However, the Petitioner argues that one of ordinary skill would modify Senzaki's CVD process in view of Min and Shin. Petition at 47.

A. A POSA Would not have been Motivated to Combine Senzaki, Min, and Shin to Arrive at the Process Recited by Claim 8 of the '016 Patent

1. A POSA would know that changes in alkyl groups of a precursor could cause non-linear unpredictable effects

The Petitioner argues that a person of ordinary skill would have been motivated to combine Senzaki in view of Min and Shin because

tetrakis(ethylmethyldamino) zirconium (“TEMAZ”) only differs from a precursor disclosed in Senzaki by one alkyl group. Petition at 48.

The Petitioner, however, ignores that the change of an alkyl group can result in unpredictable changes in the properties of a compound. Gladfelter Decl. at ¶220. For example, Dr. Gordon’s own work shows the nonlinear and unpredictable behaviors that result from changes in precursor compounds. For example, Dr. Gordon’s paper published in 2000 and entitled, “Volatile liquid precursors for the chemical vapor deposition (CVD) of thin films containing tungsten,” shows in its Table 1 the nonlinear relationship of melting point of ligands with different alkyl groups. *See* Ex. 2116, Gordon; Gladfelter Decl. at ¶220. Further, Table 1 of the ’016 Patent confirms the unpredictable nature of a substitution of an alkyl group ligand on certain properties of a compound. Two homologs of $\text{Hf}(\text{NEtMe})_4$, $\text{Hf}(\text{NEt}_2)_4$ and $\text{Hf}(\text{NMe}_2)_4$, are noted therein. These compounds differ from $\text{Hf}(\text{NEtMe})_4$ by only one alkyl substituent. However, $\text{Hf}(\text{NEt}_2)_4$ is a liquid while $\text{Hf}(\text{NMe}_2)_4$ is a solid. Thus, even close homologs of a precursor can exhibit different and unpredictable phase behaviors which could affect a precursor’s applicability for use in a process for forming a metal oxide film in a self-limiting ALD process. Gladfelter Decl. at ¶220. A POSA would know that there is a substantial degree of unpredictability in the pertinent area of chemical precursor design. *See* Section II.B, above; Gladfelter Decl. at ¶221.

Thus, a POSA could not predict with any reasonable degree of confidence whether any given precursor compound or type would lead to a successful atomic layer deposition. Gladfelter Decl. at ¶222.

2. A POSA would know that CVD disclosures do not ensure success in an ALD process

The Petitioner argues that POSA would have been motivated to combine Senzaki in view of Min and Shin because Shin teaches that tetrakis(ethylmethylamino) zirconium may “neutralize” shortcomings of its diethylamino variant. Petition at 49.

A POSA would not be motivated to attempt the proposed combination because, for example, the POSA would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD. Gladfelter Decl. at ¶224.

As stated above, Shin is directed to CVD and makes no mention of ALD. Shin at 6; Gladfelter Decl. at ¶225. There are significant differences between CVD and ALD processes, and hence, precursors that may be suitable for a CVD process are not necessarily suitable for use in an ALD process. Gladfelter Decl. at ¶225. In fact, in 2006, a study concluded that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD. *See* Ex. 2102; Gladfelter Decl. at ¶225. Furthermore, the fact that Shin is

using ethylmethylanino compounds to form metal nitrides would discourage a POSA from using such a compound to form metal oxide insulators because such a person would be concerned about nitrogen contamination. Gladfelter Decl. at ¶¶122-29.

Thus, a POSA would not be motivated to use tetrakis(ethylmethylanino) zirconium in any ALD processes described in Senzaki and Min based on the CVD benefits taught in Shin. Gladfelter Decl. at ¶226.

3. A POSA would not have had a reasonable expectation of success in using tetrakis(ethylmethylanino) zirconium in an ALD process

The Petitioner argues that a POSA would have had a reasonable expectation of success in modifying Senzaki's process in view of Min's self-limiting ALD process using tetrakis(ethylmethylanino) zirconium as taught in Shin. Petition at 49. Particularly, the Petitioner argues that a person of ordinary skill would have had a reasonable expectation of success "because Min teaches that one of the precursors specifically described in Shin successfully achieves self-limiting ALD." *Id.* The Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD. Gladfelter Decl. at ¶227.

A POSA would not have modified Senzaki's process, with Shin's CVD precursor in view of Min due to the unpredictable nature of ALD and CVD processes. Gladfelter Decl. at ¶228. One of ordinary skill would have known that

there is no reasonable expectation that a CVD precursor can be successfully adapted to ALD. *See* Section II.B, above; Gladfelter Decl. at ¶228. Min itself found that films deposited by CVD were different than those deposited by ALD. *See* Min at 8 (identifying that TiN films deposited using TEMAT and NH₃ in an ALD process were different than those deposited in a CVD process). Further, as noted by the Petitioner, Min is directed to tetrakis(ethylmethyldamino) titanium and Petitioner agrees that Min does not disclose tetrakis(ethylmethyldamido)zirconium as recited in Claim 8. *See* Petition at 45 and Min at 7. Just because one CVD precursor described in Shin was found to be successful in achieving self-limiting ALD, it does not mean that the rest of the CVD precursors in Shin will work in ALD, nor does it mean that a POSA would have had a reasonable expectation of success for the use of Shin's CVD precursors in a self-limiting ALD process based on the reasons above. Gladfelter Decl. at ¶228.

4. A POSA would not have found the proposed combination to be routine

The Petitioner argues that “it would have been routine for one of ordinary skill to” modify Senzaki with Min in view of Shin to perform an ALD process in a self-limiting manner to form a metal oxide film using tetrakis(ethylmethyldamido)zirconium. Petition at 50. Particularly, the Petitioner points to Min's teachings on the process of optimizing deposition conditions so as

to achieve self-limiting deposition as well as Shin's teaching that tetrakis(ethylmethyamido)zirconium "can be made easily[.]" *Id.* at 50, *see also* Shin at 7-9 (CVD precursor preparation). Here again, the Petitioner ignores the differences between CVD and ALD. Gladfelter Decl. at ¶229.

First, a POSA would not have modified the cited Senzaki CVD processes in view of Min and the Shin CVD precursor due to the unpredictable nature of ALD and CVD processes. *See* Section II.B, above; Gladfelter Decl. at ¶230. As detailed above at length, one of ordinary skill would have known that a CVD precursor cannot be predictably adapted to ALD due to their different requirements. *Id.* As discussed above, the metal centers themselves, combined with alkyl groups, and their different branching, can influence thermal and chemical properties of precursors in subtle ways. Gladfelter Decl. at ¶230. Thus, a POSA would understand that nonlinear and unpredictable behaviors can result from changes in precursor compounds. *Id.*

Second, with regard to Shin's teaching that tetrakis(ethylmethyamido)zirconium "can be made easily", the ease of synthesis of a compound does not have any bearing on whether it would have been a suitable precursor for use in a self-limiting ALD deposition of metal oxide films as required by the claim. Gladfelter Decl. at ¶231.

Thus, a POSA would not have expected that modifying the cited CVD deposition examples in Senzaki in view of Min with the CVD precursor of Shin would yield predictable results or would have been routine to implement as a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD. Gladfelter Decl. at ¶232.

VII. CONCLUSION

For all the reasons stated above, Patent Owner submits that the Petitioner failed to meet its burden to prove invalidity of any of Claims 1, 2, 7, 8, and 10 of the '016 Patent. Patent Owner, therefore, respectfully requests that the Board confirm Claims 1, 2, 7, 8, and 10 of the '016 Patent and that a certificate confirming the patentability of these claims be published.

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CERTIFICATION UNDER 37 C.F.R. § 42.24(d)

Under the provisions of 37 CFR § 42.24(d), the undersigned hereby certifies that the word count for the foregoing Patent Owner's Response totals 12,472, which is less than the 14,000 allowed under 37 C.F.R. § 42.24(a)(1), (b)(2).

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CERTIFICATE OF SERVICE

I hereby certify that on October 30, 2017, a true and accurate copy of this paper, PATENT OWNER'S RESPONSE and its Exhibits were served on the following counsel for Petitioner via email:

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