

By: Reza Mollaaghababa
Pepper Hamilton LLP
125 High Street
19th Floor, High Street Tower
Boston, MA 02110
(617) 204-5100 (telephone)
(617) 204-5150 (facsimile)

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 PRELIMINARY RESPONSE
PURSUANT TO 37 C.F.R. § 42.107**

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PATENT OWNER'S TABLE OF EXHIBITS

Exhibit No.	Exhibit Description
2101	Declaration of Wayne L. Gladfelter, Ph.D. in Support of Patent Owner's Preliminary Response
2102	Jones, A.C., et al., <i>MOCVD and ALD of High-K Dielectric Oxides Using Alkoxide Precursors</i> , 12 Chem. Vap. Deposition 83-98 (2006) ("Jones")
2103	Fix, R. M., 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	Ishihara, K. et. al., <i>Characterization of CVD-TiN Films Prepared with Metalorganic Source</i> , 29 No. 10 Jpn. J. Appl. Phys. 2103-05 (1990) ("Ishihara")
2105	Dubois, L.H. 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 No. 12 J. Electrochem. Soc. 3603-09 (1992) ("Dubois '92")
2106	Dubois, L.H., <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	Herlin, N. 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 (1992)("Herlin")
2110	Bechamp, K. et. al., <i>A Combined Electron Paramagnetic Resonance and Fourier Transform Infrared Study of the Co(C₆H₆)_{1,2} Complexes</i>

Exhibit No.	Exhibit Description
	<i>Isolated in Neat Benzene or in Cryogenic Matrixes</i> , 110 J Phys Chem. 6023-31 (2006) (“Bechamp”)
2111	Tiers, G.V.D., <i>Proton Nuclear Resonance Spectroscopy. I. Reliable Shielding Values by “Internal Referencing” with Tetramethysilane</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. 15-21 (2011) (“Hämäläinen”)
2113	Zaera, F., <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 No. 11 J. Electrochem. Soc., Solid-State Science and Technology 1545-49 (1975) (“Sugiyama”)
2115	Provine, J; 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, Liquid Precursor Mixtures for Deposition of Multicomponent Metal Containing Materials (Apr. 20, 2017), https://register.epo.org/application?number=EP00114321&lng=en&tab=main .

Exhibit No.	Exhibit Description
2119	U.S. Patent No. 6,238,734, Liquid Precursor Mixtures for Deposition of Multicomponent Metal Containing Materials

Pursuant to 37 C.F.R. § 42.107, the Patent Owner, President and Fellows of Harvard College (“Harvard”) hereby submits the following Preliminary Response to the Petition seeking *inter partes* review of U.S. Patent No. 8,334,016 (“the ’016 Patent”). This filing is timely under 35 U.S.C. § 313 and 37 C.F.R. § 42.107, as it is being filed within three months of the mailing date of the Notice of Filing Date Accorded to the Petition (Paper 3), mailed January 31, 2017.

I. INTRODUCTION

The Petition fails to show a reasonable likelihood of prevailing on any of the challenged claims of the ’016 Patent. Accordingly, Harvard respectfully requests that the Patent Trial and Appeal Board (“the Board”) deny *inter partes* review as to all grounds set forth in the Petition.

II. ALLEGED GROUNDS

The Petition challenges claims 1-2, 7-8, and 10 of the ’016 Patent on the following alleged grounds:

1. Claims 1-2, 7, and, 10 as being obvious over U.S. Patent No. 6,537,613 of *Senzaki et al.* (Ex. 1005, “*Senzaki*”) in view of an article by J. Min, entitled “*Atomic Layer deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethylamino)-Titanium and Ammonia*” (Ex. 1006, “*Min*”); and

2. Claim 8 as being obvious over *Senzaki* in view of *Min* and Korean Patent KR0156980, entitled “Compound for the Metal Nitride Thin Film Vapor Deposition and Deposition Method thereof” (Ex. 1007, “*Shin*”).

Petitioner fails to demonstrate a reasonable likelihood that any of the challenged claims of the '016 Patent are anticipated or rendered obvious by the cited art. *See* 37 C.F.R. § 42.108(c). Should the Board decide to institute a trial, Patent Owner reserves the right to present additional arguments as to the patentability of the claims for which trial is instituted.

III. OVERVIEW OF THE TECHNOLOGY AND THE '016 PATENT

A. Technology Background

The inventions of the '016 Patent relate to methods of depositing films via deposition processes such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). Ex. 1001 at 1:30-32; Ex. 2101, Decl. of Wayne L. Gladfelter, Ph.D. in Support of PO's Prelim. Resp. ¶24 (“Gladfelter Decl.”). Claims 1-3 and 5-10 of the '016 Patent, currently at issue, specifically relate to the use of metal amides in a self-limiting ALD process to deposit a metal oxide film. Gladfelter Decl. at ¶24, Ex. 1001 at 30:9-26 (Claim 1).

The patented inventions relate to the processes and materials used in the deposition of films on surfaces, such as thin films deposited in the manufacture of

microelectronics. Gladfelter Decl. at ¶ 25; Ex. 1001 at 2:48-52. Each of these deposition methods requires chemical reactions to form films on a surface.

Gladfelter Decl. at ¶ 25; Ex. 1001 at Abstract, 1:38 – 2:3.

ALD is a deposition process characterized by alternately exposing a heated surface to two or more reactant vapors. Gladfelter Decl. at ¶ 27; Ex. 1001 at 1:48-49. In ALD, the alternate exposure keeps the reactant vapors separate from one another when exposed to the heated surface (i.e., the reactant vapors are introduced one at a time). Gladfelter Decl. at ¶ 27. Generally, to maintain their separation, the reaction chamber containing the heated surface is purged of any excess reactant vapor before each new reactant vapor is introduced. Gladfelter Decl. at ¶ 27. For suitable reactants, ALD can provide improved step coverage and thickness uniformity compared to CVD. Gladfelter Decl. at ¶ 27; Ex. 1001 at 1:50-53.

1. Chemical Vapor Deposition

In a CVD process, reactant vapors are selected that will allow for the continuous growth of a thin film on a heated surface. Gladfelter Decl. at ¶ 28, Ex. 1001 at 1:37-48. In CVD, one or more reactant vapors are introduced into a reaction chamber, also referred to as a deposition chamber, which contains a heated surface, often referred to as a substrate. Gladfelter Decl. at ¶ 28, *see also* Ex. 1001 at 1:37-2:3; 2:26-29.

2. Atomic Layer Deposition

In an ALD deposition process, at least two reactant vapors are selected that will allow for the controlled, stepwise growth of a thin film on a heated surface. Gladfelter Decl. at ¶ 30; *see also* Ex. 1012 at 13, Ex. 1001 at 20:56-21:8, 23:54-60, 24:8-15, 24:28-36, 26:44-27:9, 27:45-30:7. In ALD, reactant vapors are alternately exposed to a heated surface in the deposition chamber. *Id.* Fundamental to ALD is the requirement that the reactant vapors react in a self-limiting manner. Gladfelter Decl. at ¶ 30; *see also* Ex. 1012 at 13. In ALD, when a first reactant vapor is exposed to a heated surface the first reactant vapor will react with available sites on the surface, forming deposits. *See* Gladfelter Decl. at ¶ 30, 32-37; *see also* Ex. 1001 at 20:56-40. Because the first reactant vapor does not react with its deposits, over time, the surface will become saturated and the reactions will stop. *See* Gladfelter Decl. at ¶ 30, 32-37; *see also* Ex. 1001 at 19:34-36; 22:20-26; 27:10-23. Once the deposition chamber is cleared of first reactant vapors and reaction by-products, a second reactant vapor is introduced. *See* Gladfelter Decl. at ¶ 30, 32-37; *see also* Ex. 1001 at 20:56-21:8, Ex. 1012 at 13. The second reactant vapor reacts with the surface sites, now containing the deposited first reactant vapor, and again, over time, the surface will become saturated and the reactions will stop. *Id.* The reactant vapors are selected such that cycles of the alternate exposure of a heated surface to the reactant vapors will result in a film formed by controlled layering of deposits. *Id.*

The Petition misleadingly states that ALD techniques were “well known” at the time of the inventions in the late 1990’s. Gladfelter Decl. at ¶ 39; *see also* Paper 1 at 7. However, as Dr. Gladfelter indicates, it is more accurate to note that although ALD was developed in the seventies in Finland, by the late 90’s there were “a lot of challenges and development work to be done before ALD” could be accepted for microelectronics. *See* Gladfelter Decl. at ¶ 39; *see also* Ex. 1012 at 13, 21-22. Specifically, work needed to be done in precursor chemistry development. *Id.*

Additionally, the Petition incorrectly states that “[b]efore 2000, the art had described and/or taught ALD to form metal oxides using metal dialkylamide precursors.” Gladfelter Decl. at ¶ 40; *see also* Paper 1 at 11-12. This statement is simply not true. *See* Gladfelter Decl. at ¶ 40; *see also* Ex. 1002 at 24.

Further, the Petitioner provides a misleading statement regarding what was known by those of skill in the art by the mid-1990s. *See* Gladfelter Decl. at ¶ 41. Specifically, Petitioner asserts that “metal dialkylamides possessed qualities that made them desirable precursors for ALD processes.” Paper 1 at 12-13 (identifying precursor volatility, thermal stability, and high reactivity as desirable characteristics for ALD). As discussed in Dr. Gladfelter’s declaration, although these characteristics are desirable, a person of ordinary skill in the art would know

that they are not indicative of whether a specific precursor would be suitable for CVD or ALD. Gladfelter Decl. at ¶ 41.

The Banerjee Report misleadingly states that a person of ordinary skill in the art at the time of the invention, when tasked with forming metal oxides with ALD, “often looked to precursors that had been successfully used in CVD processes to form metal oxides.” Gladfelter Decl. at ¶ 45; *see also* Ex. 1003 at ¶72. This implies a false premise that CVD and ALD precursors were interchangeable. Gladfelter Decl. at ¶ 45. While precursors for both CVD and ALD share practical similarities, including the need for volatility, storage stability, and safety, it was widely known that the requirements of ALD precursors are different from CVD precursors. Gladfelter Decl. at ¶ 45; *see also* Ex. 1012 at 13, Ex. 2102 at 83. There are many examples of CVD precursors that turn out not to be effective for ALD. Gladfelter Decl. at ¶ 45; *see also* Ex. 2102.

B. 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. Gladfelter Decl. at ¶ 46; *see also* Ex. 1001 at 1:22-28.

The claimed inventions are directed to atomic layer deposition (“ALD”). Gladfelter Decl. at ¶ 47; *see also* Ex. 1001 at 30:9-44. 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 chlorides and metal 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; *see also* Ex. 1047 at 3; Ex. 1032 at 6-7; Ex. 2107; Ex. 2108; Ex. 1003 at ¶ 69. Not only must the capacitance values remain at a certain level despite the reduction in size, the precursors must be delivered deep into the trenches without a premature reaction that would preclude uniform coverage within the entire deep trench structure. *Id.*

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. 2108. 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.

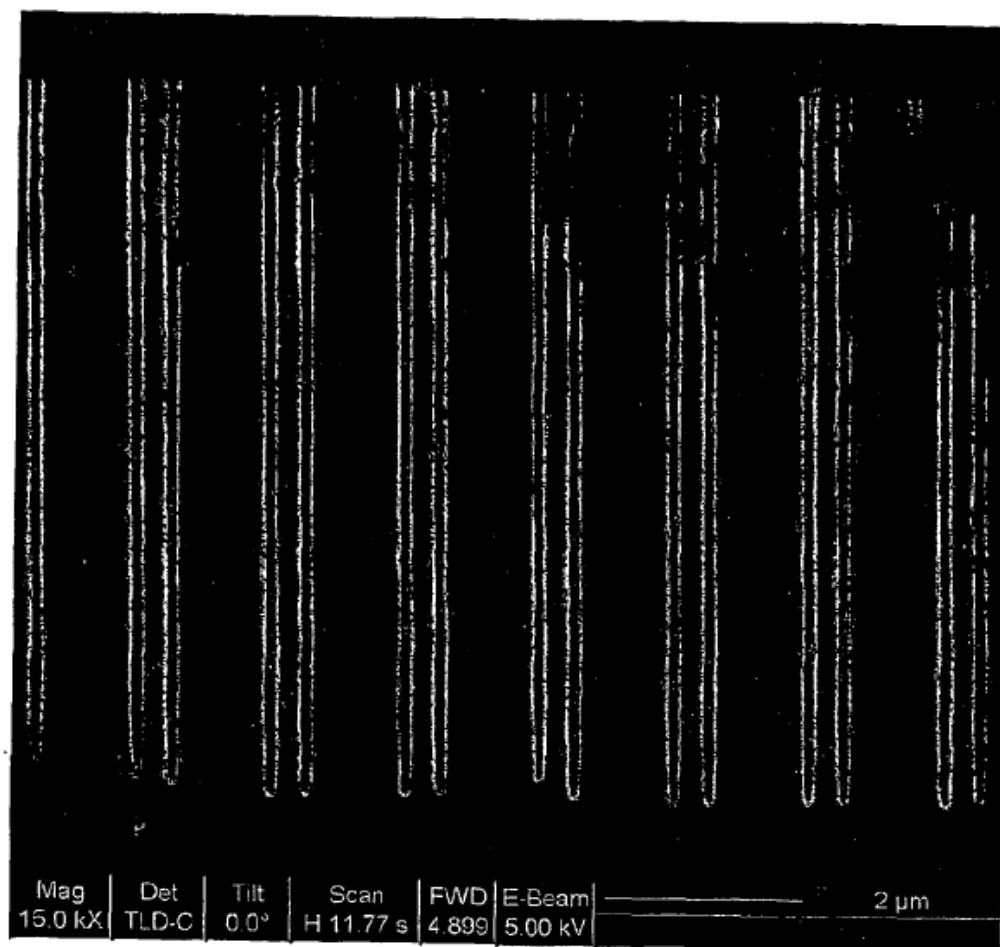
Gladfelter Decl. at ¶ 49.

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, 309-44.

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. Gladfelter Decl. at ¶ 51; *see also* Ex. 1001 at 6:33-35.

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; *see also* Ex. 1001 at 19:41-48.

IV. STATE OF THE ART OF THE TIME OF THE '016 PATENT

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. Precursor Chemistry in ALD Processes was Known to be Unpredictable

A person of ordinary skill in the art 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.

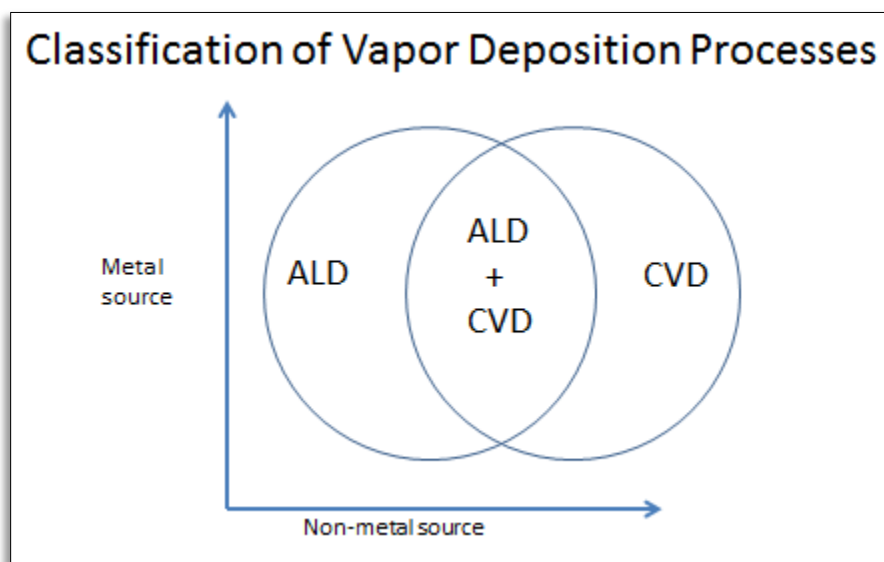
Those of ordinary skill in the art recognized that even pre-process calculations regarding theoretical ALD process reactions are not sufficient to determine whether an ALD process will be successful. *See* Gladfelter Decl. at ¶ 111; Ex. 1008 at 20. For example, those of skill in the art understood that, 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 id.*

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 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. ¶¶ 115-121. 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 at 83-98.

The diagram below visually depicts how a person of ordinary skill in the art 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.



For example, tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, is a known CVD precursor for deposition of silicon carbide (SiC), at temperatures greater than 900°C . Gladfelter Decl. at ¶117; Ex. 2109, Herlin. However, the thermal stability and lack of reactivity of tetramethylsilane render it useless as an ALD precursor. Gladfelter Decl. at ¶117. The thermal stability and lack of reactivity of tetramethylsilane is so

great that it was chosen decades ago to be the standard reference compound in Nuclear Magnetic Resonance (NMR) spectroscopy. Gladfelter Decl. at ¶117; Ex. 2111, Tiers at 1151-52. A person of ordinary skill in the art would know that these alkylsilane “preferred precursors” would not work with ALD because they do not chemisorb onto surfaces, a process required for ALD. Gladfelter Decl. at ¶117.

As an additional example, commercial copper precursor CupraSelect® is found to be suitable for CVD processes but not for ALD processes. Gladfelter Decl. at ¶120.

Further, trimethylaluminum (TMA) is well-known to function in an ALD reaction when a heated surface is alternately exposed to TMA and water vapor to deposit films of aluminum oxide. Gladfelter Decl. at ¶ 121. However, TMA cannot be used in a CVD process together with water to deposit films of aluminum oxide. *Id.*

B. 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.

V. 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, but reserves its right to provide clarification should a trial be instituted in this case.

B. A Person of Ordinary Skill In The Art

For the purposes of this paper, Patent Owner applies Petitioner's proposed definition without prejudice. Should a trial be instituted, Patent Owner reserves the right to present evidence and arguments as to the above definition or an alternative definition as to the level of ordinary skill in the art.

VI. THE CHALLENGED CLAIMS ARE NOT OBVIOUS OVER SENZAKI IN VIEW OF MIN

Petitioner alleges that claims 1-2, 7, and 10 are obvious over Senzaki in view of Min. However, as discussed below, Petitioner has failed to demonstrate a reasonable likelihood that any of the challenged claims are rendered obvious.

A. Summary of the Asserted References

1. 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. Ex. 1005 at Abstract. The process of Senzaki further includes varying the temperature of deposition from a first temperature to a second distinct temperature to result in the compositional gradient. Ex. 1005 at Abstract; 2:33-57; 3:40-46; and 6:27-34; *see also* Gladfelter Decl. at ¶ 171.

Senzaki 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. Gladfelter Decl. at ¶ 172; Ex. 1005 at 3:3-6. Senzaki states that it is “preferable” to vary the temperature during deposition in a constant manner from a low starting temperature to a high ending temperature. Gladfelter Decl. at ¶ 173; Ex. 1005 at 4:25-28.

Each of the examples provided in Senzaki is a CVD process. Gladfelter Decl. at ¶ 174; *see also* Ex. 1005 at 5:10-6:21 (Examples 1-4). Further, in each of the examples in Senzaki, the deposition temperature is purposely varied. *See id.* (“between 280 and 430°C”; “between 300 and 360°C”; “between 300 and 435°C”; and “between 310 and 350°C”).

The varying deposition temperatures in the Senzaki examples resulted in varying deposition rates. Gladfelter Decl. at ¶ 175; *see also* Ex. 1005 at 5:10-6:21 (Examples 1-4). (“the deposition rate increased from 450 to 560 angstroms per minute”; “the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute” and “deposition rate ranged from 285 to 320 angstroms per minute”). *Id.*

The substantial majority of the teachings of Senzaki relating to the precursor mixtures for deposition of multicomponent metal containing materials were

previously considered by the USPTO during the examination of the '016 Patent application in the form of European Patent EP 1067595. *See* Ex. 2117 '016 File History at 3; *see also* Ex. 2118, Senzaki EP priority. This reference is a EP application that claims priority to U.S. Patent No. 6,238,734 ("734 Patent"). The '734 patent is assigned to Air Products and Chemicals just like the Senzaki patent and it lists Yoshihide Senzaki and John Norman as inventors who are also inventors on the Senzaki patent. The '734 patent was filed approximately 9 months prior to the Senzaki patent and although the Senzaki patent does not claim priority to the '734 patent, the earlier '734 patent discloses the preferred solventless precursor mixtures of the Senzaki patent. The alleged teaching in the Senzaki patent of the claim elements "wherein the first reactant component comprises a metal alkylamide" and "wherein said insulator comprises oxygen and the metal from the metal alkylamide" is also contained in the earlier '734 patent EP publication that was considered by the Patent examiner. *See* Ex. 2119 Senzaki '734 at Col. 7, ll. 6-8; Col. 6, ll. 48-50 and ll. 55-59.

The Petitioner incorrectly asserts, in its description of Senzaki, that Senzaki states that the film formed by CVD in example 1 could also be formed by ALD. Gladfelter Decl. at ¶ 176; Paper 1 at 24. Senzaki does not state that the precursors used in its example 1 can be used for both CVD and ALD, but rather asserts that certain precursors could be used with CVD "or" ALD without specifying which

precursors would be suitable for use in an ALD process. Gladfelter Decl. at ¶ 176; Ex. 1005 at 4:4-9.

Finally, the Petitioner refers to Examples 1 and 2 of Senzaki, and asserts that the examples teach that the same precursor mixture can be used to form both nitride and oxide films. ‘664 Petition at 24; Ex. 1005 at 5:10-58. As an initial matter, these examples include mixtures of two precursors, and not a single precursor. Gladfelter Decl. at ¶ 177. Further, given the unpredictability of precursor chemistry, it is not possible to generalize that any precursor can be used to form any desired film. *Id.* Moreover, these examples of Senzaki are directed to CVD processes, and not ALD. *Id.* As discussed above, it is not possible to predict with any reasonable degree of confidence which precursors may be appropriate to form desired film via an ALD process. *Id.*

2. Jae-Sik Min, et al., Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethyamino)-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(ethylmethyamino)titanium (Ti[N(C₂H₅CH₃)₂]₄ aka “TEMAT”) and ammonia (NH₃). Gladfelter Decl. ¶ 61; *see also* Ex. 1006 at Abstract. 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. Gladfelter Decl.¶ 61; *see also* Ex. 1006 at Abstract, 8. Specifically, Min found that TiN ALD required a definite temperature range between 170°C and 210°C. Gladfelter Decl.¶ 61; *see also* Ex. 1006 at 8. The definite temperature range is required to prevent TEMAT from decomposing thermally so that a monolayer can be chemisorbed on the surfaces. *See id.*

B. The Petition Fails to Meet Its Burden to Demonstrate a Reasonable Likelihood 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). Here, Petitioner must demonstrate a reasonable likelihood that Claims 1, 2, 7 and 10 of the '016 Patent would have been unpatentable in view of the combination of Senzaki and Min. *See* 37 C.F.R. § 42.108(c). 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 person of ordinary skill in the art, 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 to 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 person of ordinary skill in the art would have been motivated to change the cited CVD process described in the examples of Senzaki to an ALD process to control film thickness. Paper 1 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. Ex. 1005 at Abstract; 2:33-57; 3:40-46; 5:10-6:21; and 6:27-34; *see also* Gladfelter Decl. at ¶ 182-186. Further, Senzaki teaches that varying deposition temperatures of its precursor mixtures results in

varying deposition rates. Ex. 1005 at 5:10-6:21. In other words, Senzaki 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 Senzaki in favor of an entirely different process. Gladfelter Decl. at ¶ 186. This argument impermissibly relies on hindsight, using the claims of 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 person of ordinary skill in the art would be motivated to reject the CVD teachings of Senzaki, 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. Paper 1 at 37-42. Petitioner has made no showing that there is a reasonable likelihood of success in doing so. *See generally* Paper 1 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 Corp.*

v. Johnson & Johnson, Inc., 679 F. Supp.2d 539, 557 (D. Del. 2010) (noting that “the chemical arts have long been acknowledged to be unpredictable”); *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) (“[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.

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

A person of ordinary skill in the art 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.

Petitioner all but admits that Senzaki does not disclose the subject matter of Claims 1, 2, 7, and 10. *See* Gladfelter Decl. at ¶ 179; Paper 1 at 29, 33, and 37. 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; Paper 1 at 29. Senzaki does not

disclose any ALD process using a metal alkylamide to form a metal oxide layer.

Gladfelter Decl. at ¶¶ 179-180; *see also* Paper 1 at 29, and 37.

In an attempt to cure the deficiencies with Sensaki, Petitioner argues that one of ordinary skill would modify Sensaki's CVD examples in view of Min. *See* Gladfelter Decl. at ¶ 181; Paper 1 at 37. However, as discussed in more detail below, a person of ordinary skill in the art would not have combined the teachings of Sensaki 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. A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Sensaki and Min to Arrive at the Process Recited by Claim 1 of the '016 Patent

a. A person of ordinary skill in the art would see that Sensaki and Min have directly contrary goals

The Petitioner argues that a person of ordinary skill would have been motivated to combine Sensaki with Min because both references teach the same goals of precisely controlling the film thickness. '664 Petition at 38-39.

Specifically, the Petitioner argues that a person of ordinary skill in the art "would have been motivated to implement Min's self-limiting teachings to achieve the goals of Sensaki 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.

First, a person of ordinary skill in the art 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; Ex. 1005 at Abstract; 2:33-57; 3:40-46; and 6:27-34. Further, 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. Ex. 1005 at 4:25-28. Each of the examples in Senzaki purposely varies the deposition temperatures. See *Id.* 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”).

Second, a person of skill in the art would recognize that the Senzaki goal of varying deposition temperatures of precursor mixtures results in varying deposition rates as shown in Senzaki’s examples. Gladfelter Decl. at ¶ 184; See Ex. 1005 at 5:10-6:21. (“the deposition rate increased from 450 to 560 angstroms per minute”; “the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute” and “deposition rate ranged from 285 to 320 angstroms per minute”).

Third, as the Petitioner indicates, Min teaches as a goal self-limiting deposition as a distinct characteristic of an ALD process. ‘664 Petition at 38; *see*

also Ex. 1006 at 9 (left). Further, Min teaches, and one of ordinary skill in the art would understand that in the desired goal of self-limiting deposition, “film thickness per cycle is independent of substrate temperature.” Gladfelter Decl. at ¶ 185; Ex. 1006 at 8 (right).

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. In fact, Fig. 3 of Min depicts such an ALD window in which the deposition rates is independent of deposition temperature. This is at odds with Sensaki. Modifying Sensaki based on Min to carry out the deposition in an ALD window as shown in Min would not allow changing the deposition rate desired by Sensaki as the deposition rate would be independent of the deposition temperature within the ALD window. Thus, a person of ordinary skill in the art would not have been motivated to combine Sensaki with Min to obtain a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD because Sensaki and Min have directly conflicting goals regarding temperature control, deposition rates, and their associated effects on controlling the thickness of the film. *Id.*

- b. A person of ordinary skill in the art would not have understood modifying Sensaki’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.” ‘664 Petition at 39. Particularly, the Petitioner points to Senzaki’s CVD example processes utilizing precursor mixtures containing a metal alkylamide and argues that one of ordinary skill in the art would be motivated to modify them based on Min’s teachings. *Id.* at 40, see also Ex. 1005 at 5:11-58 (examples 1 and 2). The Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min’s disclosure of ALD. Gladfelter Decl. at ¶ 187.

First, a person of ordinary skill in the art 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 IV.A, above; Gladfelter Decl. at ¶ 188, 119-121. One of ordinary skill would have known that a CVD process cannot be predictably adapted to ALD. *See* Section IV.A, 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* Ex. 1006 at 8. Additionally, as discussed above, a person of ordinary skill in the art 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. As explained by Dr. Gladfelter, one of ordinary skill in the art 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. Ex. 1005 at 4:8-15; Gladfelter Decl. at ¶ 189.

Second, a person of ordinary skill in the art 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 person of ordinary skill in the art considering Senzaki in view of Min would have had no reasonable expectation that the cited Senzaki CVD processes could be modified based on Min’s specific ALD process. *Id.*

A person of ordinary skill in the art 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 ¶ 191; Ex. 1006 at Abstract. A person of ordinary skill in the art 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* Ex. 1006 at 10; Gladfelter Decl. at ¶ 191.

A person of ordinary skill in the art 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 person of ordinary skill in the art 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 IV.A, above; Gladfelter Decl. at ¶ 192, 119-121

Thus, a person of ordinary skill in the art 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 person of ordinary skill in the art 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.” ‘664 Petition at 40. Petitioner’s argument ignores the state of the art at the time of Senzaki, Min and the ’016 Patent. *See* Section IV.A, above; Gladfelter Decl. at ¶ 194. A person of skill in the art 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 person of ordinary skill in the art 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 IV.A, 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 IV.A, above; Gladfelter Decl. at ¶ 196.

d. A person of ordinary skill in the art 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 person of ordinary skill in the art would have had a reasonable expectation of success in modifying the cited Senzaki CVD processes with Min's self-limiting ALD process. '664 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.” Ex. 1006 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 IV.A, 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 IV.A, above.

In the present case, one of ordinary skill 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 person of ordinary skill in the art 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 IV.B, 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 person of ordinary skill 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 that the person of skill in art 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." '664 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 Sensaki 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 teaching by these sections of Sensaki must be 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; ‘664 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 person of ordinary skill in the art than the references which have already been overcome in the prosecution of the ’016 application. *See* Ex.1002 at 24.

As such, a person of ordinary skill would have no reasonable expectation of success in modifying the Sensaki 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 person of ordinary skill in the art would not have found it obvious to try modifying Sensaki’s CVD process in view of Min**

Petitioner argues that for the same reasons as above, that it would have been obvious to a person of ordinary skill in the art to try the combination of Senzaki in view of Min. ‘664 Petition at 42.

As discussed above, a person of ordinary skill in the art 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 IV.A, above; Gladfelter Decl. at ¶ 210. More generally, a person of ordinary skill in the art 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.” ‘664 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 person of skill in the art would recognize that in Senzaki, varying deposition temperatures of precursor mixtures results in varying deposition

rates as shown in Senzaki's examples. *See* Ex. 1005 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. Ex. 1006 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 person of ordinary skill in the art 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.

VII. CLAIM 8 IS NOT OBVIOUS OVER SENZAKI IN VIEW OF MIN AND SHIN

Petitioner alleges that claim 8 is obvious over Senzaki in view of Min and Shin. Paper 1 at 4. However, as discussed below, Petitioner has failed to demonstrate a reasonable likelihood that the challenged claim is rendered obvious.

A. Summary of 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* Ex. 1007 at 1. Specifically, Shin is directed to forming titanium nitride (TiN) films using a CVD process. Gladfelter Decl.at ¶ 164; *see also* Ex. 1007 at 6. Shin contains no mention of an ALD process. Gladfelter Decl.at ¶ 164; *see also* Ex. 1007. Further, Shin was disclosed during the examination process of the '016 Patent and is listed on the face of the patent. Gladfelter Decl.at ¶ 164; *see also* Ex. 1001.

B. There Is No Reasonable Likelihood That Claim 8 Is Obvious Over Senzaki In View of Min and Shin

A person of ordinary skill in the art 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. '664 Petition at 45. Specifically, Petitioner indicates that Senzaki and Min do not disclose tetrakis(ethylmethyramido)zirconium. *Id.* As described above, a person of ordinary skill in the art 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 person of ordinary skill in the art 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. '664 Petition at 47.

- 1. A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Senzaki, Min, and Shin to Arrive at the Process Recited by Claim 8 of the '016 Patent**
 - a. A person of ordinary skill in the art 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. '664 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 year 2000 paper, "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 person of ordinary skill in the art would know that there is a substantial degree of unpredictability in the pertinent area of chemical precursor design. *See* Section IV.A, above; Gladfelter Decl. at ¶ 221.

Thus, a person of ordinary skill in the art 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.

b. A person of ordinary skill in the art would know that CVD disclosures do not ensure success in an ALD process

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

tetrakis(ethylmethyamino) zirconium may “neutralize” shortcomings of its diethylamino variant. ‘664 Petition at 49.

A person of ordinary skill would not be motivated to attempt the proposed combination because, for example, the person of ordinary skill in the art 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. Ex. 1007 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 ethylmethyamino compounds to form metal nitrides would discourage a person of ordinary skill in the art 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, one of ordinary skill in the art would not be motivated to use tetrakis(ethylmethlamino) zirconium in any ALD processes described in Senzaki and Min based on the CVD benefits taught in Shin. Gladfelter Decl. at ¶ 226.

c. A person of ordinary skill in the art would not have had a reasonable expectation of success in using tetrakis(ethylmethlamino) zirconium in an ALD process

The Petitioner argues that a person of ordinary skill in the art would have had a reasonable expectation of success in modifying Senzaki's process in view of Min's self-limiting ALD process using tetrakis(ethylmethlamino) zirconium as taught in Shin. '664 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 person of ordinary skill in the art 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 IV.A, above; Gladfelter Decl. at

¶ 228. Min itself found that films deposited by CVD were different than those deposited by ALD. *See* Ex. 1006 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(ethylmethyamino) titanium and Petitioner agrees that Min does not disclose tetrakis(ethylmethyamido)zirconium as recited in Claim 8. *See* ‘664 Petition at 45 and Ex. 1006 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 one of ordinary skill in the art 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.

d. A person of ordinary skill in the art 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(ethylmethyamido)zirconium. ‘664 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* Ex. 1007 at 7-9 (CVD precursor preparation). Here again, the Petitioner ignores the differences between CVD and ALD. Gladfelter Decl. at ¶ 229.

First, a person of ordinary skill in the art 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 IV.A, 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, one of ordinary skill in the art 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 person of ordinary skill in the art 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.

VIII. CONCLUSION

For all the reasons above, a trial should not be instituted in this matter. None of the grounds presented in the Petition gives rise to a reasonable likelihood of the Petitioner prevailing with respect to any of the challenged claims of the '016 Patent.

Dated: May 1, 2017

Respectfully submitted,
By: /Reza Mollaaghababa/
Reza Mollaaghababa
Pepper Hamilton LLP
125 High Street
19th Floor, High Street Tower
Boston, MA 02110
(617) 204-5100 (telephone)
(617) 204-5150 (facsimile)
Attorney for Patent Owner

CERTIFICATE OF SERVICE

I hereby certify that on May 1, 2017, a true and accurate copy of this paper,
PATENT OWNER'S PRELIMINARY RESPONSE UNDER 37 C.F.R. § 42.107,
was served on the following counsel for Petitioner via email:

Jeremy Jason Lang (jason.lang@weil.com)

Jared Bobrow (jared.bobrow@weil.com)

Dated: May 1, 2017

Respectfully submitted,

By: /Reza Mollaaghababa/

Reza Mollaaghababa

Pepper Hamilton LLP

125 High Street

19th Floor, High Street Tower

Boston, MA 02110

(617) 204-5100 (telephone)

(617) 204-5150 (facsimile)

Attorney for Patent Owner

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 Preliminary Response totals 10,140, which is less than the 14,000 allowed under 37 C.F.R. § 42.24(a)(1), (b)(1).

Dated: May 1, 2017

Respectfully submitted,
By: /Reza Mollaaghababa/
Reza Mollaaghababa
Pepper Hamilton LLP
125 High Street
19th Floor, High Street Tower
Boston, MA 02110
(617) 204-5100 (telephone)
(617) 204-5150 (facsimile)
Attorney for Patent Owner