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 IPR. No. **Unassigned**
U.S. Patent No. 8,334,016

Title: VAPOR DEPOSITION OF METAL OXIDES, SILICATES AND PHOSPHATES, AND SILICON DIOXIDE

PETITION FOR *INTER PARTES* REVIEW OF U.S. PATENT NO. 8,334,016 UNDER 35 U.S.C. §§ 311-319 AND 37 C.F.R. §§ 42.1-.80, 42.100-.123

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Ex.1025	Suntola, T., *Atomic Layer Epitaxy.* International Journal on the Science and Technology of Condensed Matter Films, 1992, Vol. 216, pp. 84-89. ("Suntola II")
Ex.1026	Smith, R., *Chemical Vapour Deposition of the Oxides of Titanium, Zirconium and Hafnium*. Advanced Materials for Optics and Electronics 10, 105-114, 2000, pp.105-114 ("Smith 2000")
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Ex.1034	Ritala, M. et al., *Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources*. Science, 2000, Vol. 288, pp. 319-321. ("Ritala II")
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Ex.1036	Niinistö, L. et al., *Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications*. Mat. Sci. and Eng., 1996, Vol. B41, pp. 23-29. ("Niinistö")
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Ex.1040	Colombo, D., *Anhydrous Metal Nitrates as Volatile Single Source Precursors for the CVD of Metal Oxide Films.* Chem. Vap. Deposition, 1998, 4, No. 6, pp. 220-222. ("Colombo")

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Ex.1046	Buchanan, D.A., *Scaling the gate dielectric: Materials, integration, and reliability.* IBM J. Res. Dev., 1999, Vol. 43 (3), pp. 245-264. ("Buchanan II")
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Ex.1053	Houssa, M. et al., *Charge trapping in very thin high-permittivity gate dielectric layers.* Appl. Phys. Lett., 2000, Vol. 77 (9), pp. 1381-1383. ("Houssa")
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1. INTRODUCTION

Pursuant to 35 U.S.C. §§ 311-319 and 37 C.F.R. §§ 42.1-.80, 42.100-.123, Micron Technology, Inc. ("Petitioner" or "Micron") hereby petitions the Patent Trial and Appeal Board to institute an *inter partes* review of claims 1-2, 7-8 and 10 of U.S. Patent No. 8,334,016, titled "Vapor Deposition of Metal Oxides, Silicates and Phosphates, and Silicon Dioxide" (Ex.1001, the "016 Patent"), and cancel those claims as unpatentable.

2. REQUIREMENTS FOR PETITION FOR INTER PARTES REVIEW

2.1. Grounds for Standing (37 C.F.R. § 42.104(a))

Petitioner certifies that the 016 Patent is available for *inter partes* review and that Petitioner is not barred or estopped from requesting *inter partes* review of the challenged claims of the 016 Patent on the grounds identified herein.

2.2. Notice of Lead and Backup Counsel and Service Information

Pursuant to 37 C.F.R. §§ 42.8(b)(3), 42.8(b)(4), and 42.10(a), Petitioner provides the following designation of Lead and Back-Up counsel.

Lead Counsel	**Back-Up Counsel**
Jeremy Jason Lang Registration No. 73,604 (jason.lang@weil.com) Postal & Hand-Delivery Address: Weil, Gotshal & Manges LLP 201 Redwood Shores Parkway Redwood Shores, CA 94065 T: 650-802-3237; F: 650-802-3100	Jared Bobrow (jared.bobrow@weil.com) *Pro Hac Vice Pending* Postal & Hand-Delivery Address: Weil, Gotshal & Manges LLP 201 Redwood Shores Parkway Redwood Shores, CA 94065 T: 650-802-3034; F: 650-802-3100

Pursuant to 37 C.F.R. § 42.10(b), Petitioner's Power of Attorney is attached.

2.3. Notice of Real-Parties-in-Interest (37 C.F.R. § 42.8(b)(1))

Petitioner, Micron Technology, Inc., is the real-party-in-interest. No other parties exercised or could have exercised control over this petition; no other parties funded or directed this Petition. *See* Office Patent Trial Practice Guide, 77 Fed. Reg. 48759-60.

2.4. Notice of Related Matters (37 C.F.R. § 42.8(b)(2))

President and Fellows of Harvard College ("Harvard") has asserted the 016 Patent and U.S. Patent No. 6,969,539 (the "539 Patent") (collectively, "the asserted patents") against Micron in a co-pending litigation, *President and Fellows of Harvard College, v. Micron Tech., Inc.*, 1:16-cv-11249 (D. Mass.) ("Co-Pending Litigation"). Harvard also has asserted the 016 Patent, the 539 Patent, and U.S. Patent 7,507,848 (the "848 Patent") in the following action: *President and Fellows of Harvard College v. GlobalFoundries U.S., Inc.*, 1:16-cv-11252 (D. Mass.).

In addition to this Petition, Petitioner is filing an additional two petitions for *Inter Partes* Review of U.S. Patent No. 8,334,016, and a petition for *Inter Partes* Review of U.S. Patent No. 6,969,539.[4]

[4] These petitions will be filed concurrently or within a few days.

The 016 Patent claims priority to U.S. Application Nos. 11/199,032 and 10/381,628 (now the 539 Patent), and U.S. Provisional Application Nos. 60/236,283 and 60/253,917. The 016 Patent does not claim priority to any foreign patent application.

The patent family to which the 016 Patent belongs contains, in addition to the 539 Patent to which the 016 Patent claims priority (as a continuation of the 848 Patent, which is a continuation of the 539 Patent) and the 848 Patent, six additional U.S. patent applications filed as continuations, continuations-in-part, or divisions. These are as follows:

- U.S. Patent Application No. 11/372,433 (filed March 9, 2006; abandoned)
- U.S. Patent Application No. 13/719,110 (filed Dec. 18, 2012; abandoned)
- U.S. Patent Application No. 14/587,909 (filed Dec. 31, 2014; abandoned)
- U.S. Patent Application No. 14/959,283 (filed Dec. 4, 2015; pending)
- U.S. Patent Application No. 14/974,399 (filed Dec. 18, 2015; pending)
- U.S. Patent Application No. 15/161,903 (filed May 23, 2016; pending)

2.5. Fee for *Inter Partes* Review

The Director is authorized to charge the fee specified by 37 C.F.R. § 42.15(a), and any other required fees, to Deposit Account No. 506499.

2.6. Proof of Service

Proof of service of this Petition on the patent owner at the correspondence address of record for the 016 Patent is attached.

3. IDENTIFICATION OF CLAIMS BEING CHALLENGED (§42.104(B))

Ground #1: Claims 1-2, 7, and 10 of the 016 Patent are invalid under (pre-AIA) 35 U.S.C. § 103(a) on the ground that they are obvious over U.S. Pat. No. 6,537,613, to Senzaki et al., entitled "Process for Metal Metalloid Oxides and Nitrides with Compositional Gradients," filed on April 10, 2000 and issued on March 25, 2003 (Ex.1005 ("Senzaki")) in view of Jae-Sik Min, et al., *Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethylamino)-Titanium and Ammonia,* Japanese Journal of Applied Physics, Vol. 37, No. 9A 1998, pp. 4999-5004 (Ex.1006 ("Min")).

Ground #2: Claim 8 of the 016 Patent is invalid under (pre-AIA) 35 U.S.C. § 103(a) on the ground that it is obvious over Senzaki in view of Min and KR0156980, entitled "Compound for the Deposition of Metal Nitride Thin Film and Deposition Method Thereof," filed on June 23, 1995 and published on January 28, 1997 (Ex.1007 ("Shin")).

These grounds are explained below and are supported by the Declaration of Dr. Sanjay Banerjee (Ex.1003, "Banerjee Decl.").

4. BACKGROUND OF TECHNOLOGY

The 016 Patent relates generally to the use of specific reactants in chemical vapor deposition ("CVD") and in a specific form of CVD that is frequently called atomic layer deposition ("ALD").[5] Ex.1001, 016 Patent, 1:29-32, 1:49-50. Both CVD and ALD are thin film deposition processes used in a number of industrial applications to deposit a solid material from reactants (also called "precursors") onto a substrate. The substrate may be, for example, a silicon wafer used in manufacturing a microelectronic device, a component of a solar cell, or film in a light-emitting diode. Ex.1003, Banerjee Decl., ¶29.

[5] Many names have been used to describe ALD, including its original name, atomic layer epitaxy ("ALE") as well as atomic layer processing, chemical vapor atomic layer deposition, digital layer epitaxy, and others. Ex.1008, Leskelä I, p.18; Ex.1003, Banerjee Decl., ¶43. However, as of the late 1990s, the term "atomic layer deposition" had become the most popular term used to describe this method. Ex.1008, Leskelä I, p.18; Ex.1003, Banerjee Decl., ¶43.

4.1. Chemical Vapor Deposition (CVD)

The basic CVD process has been in use for a very long time, having been described as early as the 19th century. Ex.1003, Banerjee Decl., ¶31. In CVD, a heated substrate, such as a semiconductor wafer, is positioned in a reaction chamber. The heated substrate is exposed to one or more vaporized reactants and, through the occurrence of chemical reactions, a thin film is deposited on the substrate surface. Ex.1001, 016 Patent, 1:38-48; Ex.1003, Banerjee Decl., ¶29. The reactants are chosen to produce the desired film. Ex.1003, Banerjee Decl., ¶29.

CVD growth control is analog because growth continues so long as there is an available supply of reactants. *Id.*, ¶35. Thus, when performing CVD, it is often difficult to achieve precise control over the thickness of the film being deposited. *Id.* Adding to the difficulty of precisely controlling film thickness is the fact that CVD reactions can occur both on the heated substrate surface and in the gas phase (that is, in the headspace above the substrate in the chamber). This can negatively affect film uniformity and must be accounted for in controlling the thickness of the growing film. *Id.*

4.2. Atomic Layer Deposition (ALD)

ALD is a type of CVD in which, rather than exposing the heated substrate to multiple vaporized reactants simultaneously, each reactant is introduced alternately

into the chamber. Ex.1001, 016 Patent, 1:48-50; Ex.1003, Banerjee Decl., ¶41. ALD was invented in the 1970s and has been in practice since that time to deposit thin films, including metal oxide films; indeed, deposition of oxides was one of the first procedures carried out by ALD when the technique was invented. Ex.1003, Banerjee Decl., ¶¶42, 55. As discussed below, in the 1990s, the industry recognized that, as microelectronic devices continued to decrease in size, silicon dioxide would need to be replaced as the preferred dielectric for semiconductor gates and capacitors. *Id.*, ¶¶66, 68. This, in turn, prompted the industry to explore ALD metal oxides as a replacement for silicon dioxide, given that ALD techniques were well known at that time. *Id.*, ¶69-72.

In an exemplary ALD scheme, a first reactant is pulsed into the reaction chamber and a layer of the first reactant is deposited on the substrate. Then a second reactant is pulsed into the chamber and reacts with the first reactant layer on the substrate to form the desired film. *Id.*, ¶44. Between reactant pulses, any remaining vaporized reactant gas from the previous pulse is evacuated from the deposition chamber (for example, by vacuum pumping or by purging the chamber with an inert gas). *Id.* In this exemplary scheme, the sequence of (1) pulsing in a first reactant, (2) evacuating the excess first reactant, (3) pulsing in a second reactant, and (4) evacuating the excess second reactant, constitutes a complete

ALD cycle. *Id.*, ¶¶44-45. This cycle is repeated multiple times until the desired film thickness is achieved. *Id.*, ¶45.

4.3. ALD of Metal Oxides to Form Gate and Capacitor Dielectrics

A well-known characteristic of ALD is that it affords precise, superior control over the thickness of the growing film as compared to CVD. *Id.*, ¶50. This is because the deposition processes occurring on the surface of the substrate in ALD can be made to be "self-limiting." *Id.*, ¶¶44-47. "Self-limiting" processes are not dependent upon the amount of reactant available. Rather, these ALD processes are limited by the availability of ligands (functional chemical groups with which a chemical reaction can occur) on the heated surface. With these self-limiting processes, when all available ligands on the surface are bound to a reactant molecule, the deposition effectively terminates even if there is still excess reactant present in the chamber. *Id.*, ¶45. Accordingly, by this self-limiting process in ALD, approximately one monolayer (an "atomic layer") of the desired film will be deposited in an ALD cycle. Put another way, growth of a film during ALD is often measured in terms of how much the film will grow per cycle; the cycle is repeated a sufficient number of times so as to achieve a film of the desired thickness. *Id.*, ¶¶46, 50. This allows for precise control of film thickness. This self-limiting characteristic directly contrasts with the analog, continuous growth in CVD, in which the deposited film will keep growing so long as there is a supply of reactants

in the chamber. *Id.* Self-limiting growth conditions in ALD are achieved by adjusting the deposition parameters, which is a routine process when performing ALD. Ex.1008, Leskelä I, p.17; Ex.1003, Banerjee Decl., ¶44.

Another benefit of ALD relates to the quality of the films it produces. Oxide films with proper stoichiometry (that is, the numerical ratio of the elements of the film to one another[6]) are desirable because they often exhibit high thermal and chemical stability as well as superior electrical properties. *Id*. The strict regulation of the delivery of reactants into the deposition chamber in ALD and the resulting atomic-layer control over the growing thin film are useful for achieving proper stoichiometry. *Id.*, ¶53; *see also* Ex.1009, Vaartstra, 1:64-2:4.

Another benefit of ALD is that ALD generally may be carried out at temperatures lower than those that are often required for CVD. Ex.1003, Banerjee Decl., ¶49. This means that a given precursor which would thermally decompose at a temperature needed for CVD may not thermally decompose at a temperature useful for ALD. *Id.*

[6] For example, a layer of aluminum oxide (Al_2O_3) ideally should have a total number of oxygen atoms that is as close as possible to 3/2 times the total number of aluminum atoms. Ex.1003, Banerjee Decl., ¶53.

By the 1990s, those of ordinary skill in the art recognized that ALD's ability to provide precise thickness control and proper stoichiometry would be advantageous in making electronic devices smaller and smaller. *Id.*, ¶71. Following Moore's Law, as microelectronic devices decreased in size, the industry recognized that it would need atomic-scale control over film thickness, particularly for features such as gate and capacitor dielectrics, and ALD was identified as a technology suitable to meet those needs. *Id.*

In particular, ALD of metal oxides was being explored during the 1990s to find a replacement for silicon dioxide as a dielectric in microelectronic devices. *Id.*, ¶¶69-72. Those in the field of microelectronic devices recognized at least by the 1990s that silicon dioxide, the most widely-used gate dielectric material used in silicon microelectronics, would not be suitable for use in nanoscale devices in the near future due to charge leakage. Specifically, due to its relatively low dielectric constant compared to high-κ dielectrics, silicon dioxide films needed to be extremely thin to maintain sufficient capacitance (which is inversely proportional to the distance between capacitor plates). *Id.*, ¶¶65, 68. As silicon dioxide film thickness decreased, however, charge leakage through the film increased to the point that using such thin silicon dioxide films was no longer feasible. *Id.*, ¶68. Thus, as the projected nanoscale devices would require much thinner films than was feasible if made of silicon dioxide, other metal oxides such as zirconium

oxide, hafnium oxide, and titanium oxide were being studied as alternatives. *Id.*, ¶¶68-69. These metal oxides have higher dielectric constants compared to silicon dioxide, such that sufficient capacitance could be maintained without requiring the film to be so thin as to induce too much charge leakage. *Id.* Further, in depositing these metal oxides in nano-scale devices, atomic-scale control of film thickness was necessary to precisely control the amount of charge leakage, which is highly dependent on film thickness. *Id.*, ¶71. ALD (with its precise thickness control and ability to deposit atomic-scale, stoichiometric films) was a natural solution for depositing these films. *Id.*

4.4. Metal Alkylamides and Metal Dialkylamides as Precursors to Form Metal-Containing Films

Many different metal precursors, such as metal halides, metal alkyls, metal alkoxides, and metal alkylamides (including metal dialkylamides), have been used in CVD and ALD processes to form metal-containing films, such as metal oxides and metal nitrides. *Id.*, ¶¶38-40, 60. Metal dialkylamides are a particular category of precursor that has been used often in the formation of thin films. *Id.*, ¶¶39-40, 62. For example, metal dialkylamides were used in CVD and ALD of metal nitride films throughout the 1990s. *Id.*, ¶¶40, 62. Metal dialkylamides also were used to form metal oxide films by CVD in the 1990s. *Id.*, ¶40. Before 2000, the art had described and/or taught ALD to form metal oxides using metal

dialkylamide precursors. *Id.*, ¶¶95-101, ¶¶115-137; *see also* Ex.1038, Buchanan, 4:22-32, 14:55-57, 19:60-21:2.

Certain precursor characteristics were known to be particularly desirable for ALD by the mid-1990s. For example, it was known that a precursor should be sufficiently volatile so as to facilitate transport as a vapor into the deposition chamber. *Id.,* ¶¶57-58. As another example, it was known that a precursor should exhibit sufficient thermal stability to avoid thermal decomposition during the ALD process. *Id.,* ¶57. As another example, it was known that a precursor should be highly reactive so as to achieve self-limiting surface deposition processes. *Id.,* ¶¶57, 59. Those of ordinary skill had known that metal dialkylamides exhibited these characteristics since the 1960s. *Id.,* ¶¶62-63. Thus, those of skill in the art recognized at least by the 1990s that metal dialkylamides possessed qualities that made them desirable precursors for ALD processes. *Id.*

5. OVERVIEW OF THE 016 PATENT

The 016 Patent was filed on March 19, 2009 and issued on December 18, 2012. The 016 Patent relates generally to the use of specific reactants used in CVD and in a specific form of CVD, namely ALD. Ex.1001, 016 Patent, 1:30-33. The 016 Patent does not purport to have invented CVD or ALD. Nor could it: at the time that the 016 Patent was filed, both CVD and ALD were well-known

techniques that had been used for many years to deposit thin films. *Id.,* 1:38-54; Ex.1003, Banerjee Decl., ¶¶31, 42.

The 016 Patent notes in the Background section that those in the field had been evaluating metal silicates to replace silicon dioxide in gate insulators in silicon semiconductor technology. Ex.1001, 016 Patent, 1:55-60. Before the 016 Patent was filed, ALD had been used, for example, to deposit metal silicates using metal chlorides and silicon alkoxides as precursors, but the deposited films included chlorine, which the 016 Patent asserts can be problematic. *Id*., 1:60-2:2. According to the 016 Patent, "it would be advantageous to have chlorine-free precursors for CVD or ALD of metal silicates and oxides." *Id.,* 2:2-3.

The 016 Patent then describes using CVD and ALD to form a variety of thin films using a variety of chlorine-free precursors and reactants. *Id.,* 7:31-32, 8:57-58, 20:32-21:8. The 016 Patent lists precursors in various tables and sets forth examples of methods of forming silicate, phosphate, and oxide films using a variety of precursors and reactants. *Id.,* 10:10-17:58 (Table 1, listing "Some Volatile Metal or Metalloid Amides"; Table 2, listing "Some Volatile Organometallic Compounds"; Table 3, listing "Some Volatile Metal or Metalloid Alkoxides"); 23:29-30:7 (exemplary methods).

Claim 1 of the 016 Patent is directed to a process for making an insulator in a microelectronic device. The process uses an ALD technique in which one of the

reactants includes a metal alkylamide and the depositions are self-limiting. The resulting film must include oxygen and the metal from the alkylamide. Claim 2, which depends on claim 1, requires that the insulator insulate a gate or a capacitor. The remaining dependent claims at issue in this petition (7-8, 10) claim various specific metal dialkylamide precursors. All of the precursors in dependent claims 7-8 and 10 include zirconium.

6. 016 PATENT PROSECUTION HISTORY

The application leading to the 016 Patent was filed on March 19, 2009. The original application included 20 claims, but Applicant cancelled claims 11-20 in response to an office action dated January 12, 2012, requiring Applicant to elect either claims 1-10 (drawn to a method) or claims 11-20 (drawn to a product). Applicant elected claims 1-10, which correspond to issued claims 1-10 respectively. Ex.1002, 016 Patent FH, pp.3-5.

On March 22, 2012, the Examiner rejected claims 1-10 under 35 U.S.C. § 103(a) as obvious over Aarik et al. (Thin Solid Films article) in view of Vaartstra (U.S. Patent No. 6,159,855). *Id.,* pp.8-11. The Examiner found that Aarik discloses ALD of hafnium dioxide using hafnium chloride as a precursor, but not a metal alkylamide precursor. *Id*. The Examiner found that it would have been obvious to perform the process taught in Aarik but with Vaartstra's metal alkylamide precursors in place of Aarik's metal chloride precursor. *Id*.

In the same office action dated March 22, 2012, the Examiner rejected claims 1-10 under the non-statutory double patenting doctrine as obvious over claims 24-31 of the 539 Patent in view of Vaartstra. *Id.,* pp.12-13. The Examiner found that the 539 Patent teaches a process for forming a metal oxide, comprising: exposing a heated surface alternately to the vapor of one or more metal amides having an amido group selected from the group consisting of dialkylamido, disilylamido and (alkyl)(silyl) amido moieties, and then to the vapors of water or an alcohol. *Id.* The Examiner found that the process taught in the 539 Patent is similar to claim 1 of the application leading to the 016 Patent, but that it fails to specifically teach a metal alkylamide. *Id*. The Examiner found that Vaartstra discloses metalloamide compound mixtures for use in chemical vapor deposition and in one embodiment, the metalloamide compounds can be a variety of compounds including tetrakis(diethylamido) hafnium and tetrakis(diethylamido) zirconium. On this basis, the Examiner found that it would have been obvious to incorporate these compounds in the process taught in the 539 Patent. *Id.*

On September 6, 2012, Applicant responded to the Examiner's rejections. Applicant amended claim 1 by adding language specifying that the "deposition of the first reactant component and the second reactant component are self-limiting." *Id.,* p.14. Applicant commented that with this amendment, claim 1 was "directed to an *alternating layer deposition (ALD)* process." *Id.,* p.16. Applicant failed to

inform the Examiner that ALD processes routinely were made to exhibit "self-limiting" deposition. Ex.1008, Leskelä I, pp.16-17; Ex.1003, Banerjee Decl., ¶44.

Applicant also argued that it would not have been obvious to combine Aarik with Vaartstra because Vaartstra's organometallic compounds are used in CVD, not ALD, and that Vaartstra does not suggest that its precursors would have provided the self-limiting growth needed in Aarik's ALD process. Ex.1002, 016 Patent FH, pp.16-18. Applicant failed to tell the Examiner, and the Examiner may not have appreciated, that metal alkylamides were well known in the field, had been characterized many years before applicant had filed its application, and were known to possess characteristics desirable in ALD precursors (e.g., volatility, an adequate temperature window between evaporation and decomposition, relatively high thermal stability, and reactivity with surface ligands). Ex.1003, Banerjee Decl., ¶¶62-63, 89. Nor did applicant inform the Examiner, and the Examiner may not have appreciated, that Vaartstra disclosed many of the same metal alkylamides that are disclosed and claimed in the 016 Patent, including tetrakis-(diethylamido)-hafnium, tetrakis-(diethylamido)-zirconium, and tetrakis-(dimethylamido)-zirconium. Ex.1009, Vaartstra, 6:19-65. Petitioner is also filing a petition seeking review of the 016 Patent in view of Vaartstra, and that petition includes important evidence and arguments that were not in front of the Examiner when considering Vaartstra.

Regarding the Examiner's double patenting rejection, applicant argued that Vaartstra does not remedy the deficiency of the 539 Patent because Vaartstra does not teach that any of the precursors it describes can provide self-limited growth during deposition, and further that there was no reason provided that one of ordinary skill in the art would have expected precursors useful in CVD as described in Vaartstra to be equally useful in ALD. Ex.1002, 016 FH, pp.16-18. Applicant failed to tell the Examiner, and the Examiner may not have appreciated, that the 539 Patent in fact discloses metal alkylamides. Ex.1020, 539 Patent, Table 1 (listing multiple metal alkylamides including $Hf(NEt_2)_4$ and $Zr(NEt_2)_4$). Similarly, the Examiner may not have appreciated that metal alkylamides were well known in the field, had been characterized many years before applicant had filed its application, and were known to possess characteristics considered desirable in ALD precursors (e.g., volatility, an adequate temperature window between evaporation and decomposition, relatively high thermal stability, and reactivity with surface ligands). Ex.1003, Banerjee Decl., ¶¶62-63, 89. Nor did applicant inform the Examiner, and the Examiner may not have appreciated, that Vaartstra disclosed many of the same metal alkylamides that are disclosed and claimed in the 016 Patent, including tetrakis-(diethylamido)-hafnium, tetrakis-(diethylamido)-zirconium, and tetrakis-(dimethylamido)-zirconium. Ex.1009, Vaartstra, 6:19-65.

Following applicant's reply, the Examiner issued a notice of allowance on October 10, 2012. While the Examiner recognized that it was well known to utilize metal alkylamide to form nitride films, the Examiner nonetheless concluded that the prior art references fail to teach or suggest using alkylamide to form a metal oxide film by ALD. Ex.1002, 016 FH, p.24. The Examiner referred in this statement not only to Vaartstra and Aarik, but further to a 1999 Applied Physics Letters article by Min and colleagues (which taught using metal alkylamide to form nitride films). *Id.,* pp.24-25.[7] In making this statement, the Examiner appears not to have appreciated, and Applicant did not inform the Examiner, that the same metal precursors in Vaartstra and the 1999 Min article were disclosed for use in depositing both oxides and nitrides. Specifically, the Examiner appears not to have appreciated that Vaartstra itself teaches that the same metal precursors for forming nitrides can equally be used to form oxides:

[7] The Min article referenced by the Examiner in his Notice of Allowance describes "Metal-organic atomic-layer deposition of titanium-silicon nitride films." Ex.1010, Min 1999, p.6. This publication describes a different process (formation of titanium-silicon nitride films by ALD) from that described in the Min reference referred to in this petition (which describes formation of titanium nitride films by ALD). *See infra* Section 9.2.

> For example, a multi-metallic nitride can be deposited by reacting the metalloamide vapor with either ammonia or hydrazine. . . . Similarly, a multi-metallic oxide can be deposited by reacting the metalloamide vapor with oxygen, nitrous oxide, water vapor or ozone.

Ex.1009, Vaartstra, 11:2-10 (emphasis added). Vaartstra further discloses that "the metalloamide compounds are versatile in that, by appropriate choice of a reactant gas, they can be used to form any of metal nitride, oxide, boride, sulfide, etc.-containing multi-metallic layers." *Id.,* 13:51-54. Accordingly, the Examiner appears to have overlooked, or not appreciated, Vaartstra's teaching that a metal alkylamide precursor may be used to form a metal oxide or a metal nitride film, with the appropriate choice of a reactant gas. In other words, Vaartstra itself teaches that an ALD process such as the 1999 Min article's, which uses a species of Vaartstra's preferred alkylamide precursors to form a titanium silicon nitride film, would be suitable to form a metal oxide with Vaartstra's precursors.

Indeed, the Examiner appears to not have been aware of other prior art references that confirm this, namely, references which teach that the same metal precursor may be used in vapor deposition processes to form either a nitride or an oxide. *See, e.g.*, Ex.1011, George, p.6 (Scheme 1, showing that $Al(CH_3)_3$ was used to form Al_2O_3 (oxide) and AlN (nitride); Ex.1008, Leskelä I, pp.21, 25 (metal chlorides as precursors to make oxide and nitride films); Ex.1012, Leskelä II,

pp.18 ("Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films."), 25-28 (a variety of precursors used in ALD to form both oxides and nitrides); Ex.1013, Bastianini, p.17 (reporting the use of $Zr(NEt_2)_4$, "which had already been successfully employed in the CVD growth of Zr_3N_4 [a nitride] in the presence of NH_3" for deposition of ZrO_2 (an oxide)).

7. CLAIM CONSTRUCTION[8]

7.1. Applicable Law

A claim subject to *inter partes* review is given the "broadest reasonable construction in light of the specification of the patent in which it appears."[9] 37

[8] Petitioner expressly reserves the right to challenge in district court litigation one or more claims (and claim terms) of the 016 Patent for failure to satisfy the requirements of 35 U.S.C § 112, which cannot be raised in these proceedings. *See* 35 U.S.C. § 311(b). Nothing in this Petition shall be construed as a waiver of such challenge, or agreement that the requirements of 35 U.S.C. § 112 are met for any claim of the 016 Patent.

[9] The district court, in contrast, affords a claim term its "ordinary and customary meaning . . . to a person of ordinary skill in the art in question at the time of the invention." *Phillips v. AWH Corp.,* 415 F.3d 1303, 1313 (Fed. Cir. 2005) (en

C.F.R. § 42.100(b). Any ambiguity regarding the "broadest reasonable construction" of a claim term is resolved in favor of the broader construction absent amendment by the patent owner. Final Rule, 77 Fed. Reg. 48680, 48699 (Aug. 14, 2012).

7.2. Construction of Claim Terms

All claim terms have been accorded their broadest reasonable interpretation as understood by a person of ordinary skill in the art and consistent with the specification of the 016 Patent.

8. PERSON HAVING ORDINARY SKILL IN THE ART

A person having ordinary skill in the art with respect to the technology described in the 016 Patent 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. *See* Ex.1003, Banerjee Decl., ¶21.

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banc). Petitioner expressly reserves the right to argue different or additional claim construction positions under this standard in district court.

9. DESCRIPTION OF THE PRIOR ART

9.1. U.S. Patent No. 6,537,613 ("Senzaki")[10]

Senzaki is directed to the same field of technology as the 016 Patent, namely, the deposition of thin films using CVD and ALD techniques. Like the 016 Patent, Senzaki notes that the formation of metal silicates had been studied in the art for use as gate dielectric films. Ex.1005, Senzaki, 1:41-65. Senzaki also notes that many other mixed metal films had been formed in the art for use as dielectrics, including metal oxides. *Id.*, 1:66-2:17. 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." *Id.*, 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.

Like the 016 Patent, Senzaki discloses CVD and ALD techniques for depositing thin electronic films, such as metal-metalloid oxide and nitride films for

[10] Senzaki was filed on April 10, 2000 and issued on March 25, 2003, and is therefore prior art at least under § 102(e). *See* Ex.1005, Senzaki. Senzaki was not cited to or by the Examiner during prosecution of the 016 Patent.

use as gate dielectrics in integrated circuit devices. Senzaki describes, for example, processes for forming a zirconium-silicon-oxide gate dielectric film by CVD. *Id.*, 3:40-53, 5:11-43. The zirconium precursor is tetrakis (diethylamido) zirconium, which is abbreviated as $Zr(NEt_2)_4$.[11] *Id.*, 3:40-42, 5:13; Ex.1003, Banerjee Decl., ¶100. This is a metal dialkylamide. Ex.1003, Banerjee Decl. ¶100. Senzaki further explains that this metal dialkylamide precursor is reacted with an oxidant to form a metal-metalloid oxide, where the oxygen source can be "oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen

[11] Petitioner notes that, when metal dialkylamides are described in the art, sometimes the suffix "amino" is used and at other times the suffix "amido" is used. *Compare* Ex.1006, Min, p.7 *with* Ex.1041, Bouman, p.10. It should be further noted that Harvard itself has used "amino" to refer to the "amido" groups present in metal dialkylamides. *See, e.g.*, Ex.1042, Harvard Complaint, ¶35 (alleging that "tetrakis(ethylmethylamino) zirconium" has an "amido group selected from the group consisting of dialkylamido, disilylamido and (alkyl)(sily[l]) amido moieties"). Thus, for example, tetrakis(diethylamido) zirconium and tetrakis(diethylamino) zirconium refer to the same compound. *See* Ex.1003, Banerjee Decl., ¶63 n.6.

peroxide, air and mixtures thereof."[12] Ex.1005, Senzaki, 4:32-37. Although Example 1 illustrates forming the metal-metalloid oxide film by CVD from a first mixture that includes a zirconium dialkylamide and a second reactant of oxygen, Senzaki states that the film could be formed by ALD instead. *Id.*, 4:4-15 ("In addition to thermal low pressure CVD, the above precursors could be used for . . . atomic layer deposition.").

Senzaki teaches that the same metal precursor, including metal dialkylamide precursors, may be used to form both oxide and nitride films with the appropriate choice of reactant gas. For example, Senzaki discloses an example in which tetrakis(diethylamido) zirconium, a metal dialkylamide, is used to form a zirconium silicon oxide film (Example 1) using oxygen gas as a reactant gas, and another example in which this same metal dialkylamide precursor is used to form a

[12] Senzaki's conditions for its CVD and ALD processes would deliver the oxidant into the deposition chamber in vaporized form. *See, e.g.*, Ex.1005, Senzaki, 5:18-20 (indicating that precursors are delivered by an injection system with a vaporization temperature of 110°C, sufficient to vaporize an oxidant such as water); Ex.1003, Banerjee Decl., ¶100. This is consistent with conventional techniques for carrying out CVD and ALD. Ex.1003, Banerjee Decl., ¶¶29, 44.

zirconium silicon nitride film (Example 2) using ammonia as a reactant gas. *Id.*, 5:44-58.

9.2. Jae-Sik Min, et al., Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethylamino)-Titanium and Ammonia ("Min")[13]

Min generally relates to using ALD to deposit thin diffusion barriers, and in particular to the use of a metal dialkylamide precursor – tetrakis(ethylmethylamino) titanium, abbreviated as TEMAT – and ammonia in alternating pulses to form a thin titanium nitride (TiN) film. Ex.1006, Min, p.7. Like the 016 Patent, Min observes that forming TiN films with chloride precursors can present corrosion and other problems. *Id.*, p.7 (left). Min also notes that some metalorganic compounds, when deposited using CVD, produce films with high resistivity and carbon contamination. *Id.*, p.7 (left).

To address these issues, and improve the quality of the deposited films, Min selected a precursor, TEMAT, that does not contain chlorine, and Min avoided the gas phase reactions between precursor and reactant that take place in CVD by using ALD instead. *Id.*, p.7 (right). Min cites three studies in which tetrakis(dialkylamino) titanium compounds, of which TEMAT is a type, were used

[13] Min was published in September 1998 and is prior art under § 102(b). *See* Ex.1006, Min.

in CVD processes to form titanium nitride films. *Id.* (left). In Min's process, a substrate was heated to between 150° C and 400° C in a warm-wall reactor; after optimization of reaction conditions, a temperature of 200° C was chosen to carry out further ALD depositions. *Id.*, pp.7 (right), 9-11. ALD occurred by exposing the heated substrate to alternate vapor pulses in the following regulated sequence: TEMAT vapor pulse, argon purge gas pulse, ammonia gas pulse, argon purge gas pulse. *Id.*, p.7 (right), p.8 (Fig. 2). This cycle was repeated until the desired film thickness was obtained. *Id.*, p.7 (right), p.8 (Fig. 2). Through this ALD process, Min reports the ability to control film thickness by controlling the number of cycles, that is, there was a linear relationship between the number of ALD cycles and film thickness. *Id.*, p.10 (right), p.11 (left) & Fig. 10.

Importantly, Min describes adjustment of its deposition conditions in order to achieve self-limiting growth. *Id.*, p.9 (left) ("These results suggest realization of a self-limiting process by adsorption of TEMAT and are distinct characteristic of ALD process."); *see also id.*, p.8 (right). Min further explained that the growth control wherein film thickness was controlled simply by the number of cycles performed was achieved because the deposition of the reactant components was self-limiting. *Id.*, p.8 (left), p.9 (right). Min also reports that using the ALD process with self-limiting growth led to the film's "morphology" being

"completely continuous," the film being nearly stoichiometric, and the film having almost no particles. *Id.*, p.11 (right) & Fig. 9.

9.3. KR0156980 ("Shin")[14]

Shin relates to precursor compounds for depositing a metal nitride film, which compounds are "advantageous in increasing deposition speed and decreasing carbon impurity." Ex.1007, Shin, p.1. As an example, Shin describes precursors for deposition of titanium nitride films including "titanium aminate," which has a general formula of $Ti(NR_2)_4$.[15] Shin further describes an increase in the use of $Ti(NR_2)_4$ compounds as a precursor during the 1990s, in place of titanium chloride which presented a number of problems as a precursor including incorporation of chlorine into the deposited film and the formation of undesirable by-products. *Id.*, pp.4-5.

Shin describes tetrakis(diethylamino) titanium and tetrakis(dimethylamino) titanium as precursors "mainly used for the deposition of titanium nitride (TiN) thin film." *Id.*, p.5. Shin further describes shortcomings of these precursors as

[14] Shin was filed on June 23, 1995 and was published on January 28, 1997. Shin was not cited to or by the Examiner during prosecution of the 016 Patent.

[15] Based on this general formula, a "titanium aminate" is a titanium dialkylamide. Ex.1003, Banerjee Decl., ¶109.

single precursors for depositing a titanium nitride film (meaning that no second reactant gas is used). These include the inclusion of carbon impurities in the deposited film, which causes an increase in resistivity that is undesirable. *Id.* Shin states that, as a result of these shortcomings of other titanium dialkylamide precursors, there was a need to develop a precursor that has "characteristics at a level comparable to tetrakise dimethyl amino amino titanium [or] tetrakise diethyl amino amino titanium" and also "can supplement[] the shortcomings of the existing single precursor." *Id.*, p.6.

The precursor disclosed by Shin to meet these criteria has a general formula of "$M[N(CH_3)C_2H_5]X$." *Id.*, p.1. In this formula, "M is selected from the metallic elements belonging to the group 3, group 4, and group 5 on the periodic table, and X is an integer between 3-5." *Id.*; *see also id.,* p. 2. This formula encompasses such compounds as tetrakis(ethylmethylamino) titanium and tetrakis(ethylmethylamino) zirconium, both of which Shin discloses specifically. *Id.*, p.7. Shin further teaches synthesis methods by which both compounds "can be made easily." *Id*. Shin teaches that compounds of its general formula $M[N(CH_3)C_2H_5]_x$ "exhibit[] intermediate characteristics of tetrakise dimethyl amino amino titanium and tetrakise diethyl amino amino titanium" such that "the problems caused by the two compounds can be neutralized more or less." *Id*.

10. GROUND #1: CLAIMS 1-2, 7, AND 10 OF THE 016 PATENT ARE UNPATENTABLE AS BEING OBVIOUS OVER SENZAKI IN VIEW OF MIN

Senzaki discloses the elements of claims 1-2, 7, and 10 of the 016 patent reciting a process for making an insulator in a microelectronic device, comprising: introducing a first reactant component into a deposition chamber; introducing a second reactant component into the deposition chamber; and alternately repeating introducing the first reactant component and the second reactant component into the deposition chamber. Senzaki further discloses the elements for 1-2, 7, and 10 of the 016 patent reciting that the first reactant comprises a metal alkylamide, that the second reactant component interacts with the deposited first reactant component to form the insulator for a gate, and that said insulator comprises oxygen and the metal from the metal alkylamide.

The only element of independent claim 1 (from which claims 2, 7, and 10 depend) that is arguably not expressly disclosed by Senzaki is the limitation "wherein deposition of the first reactant component and the second reactant component are self-limiting." While Senzaki arguably does not expressly disclose this limitation, it would have been understood by and obvious to one of ordinary skill in the art that the ALD method described in Senzaki either achieves or can be made to achieve self-limiting deposition of the first and second reactant components, particularly in light of Senzaki's disclosure that "an approximately

single layer of precursor molecules are adsorbed on a surface." *Id.*, 4:4-15. Moreover, Min discloses that in ALD, process conditions may be optimized to achieve self-limiting growth and yield the advantages of ALD, such as precise and accurate control of film thickness and film conformity, and thus, at a minimum, would have been obvious in view of Min. *See infra* Section 10.5 (describing motivations to combine Senzaki and Min).

Ground #1[16] is a non-redundant ground to the other two petitions (which are based on Buchanan and Vaartstra as the primary references) that Petitioner is filing for review of the 016 Patent for at least the following reasons. First, Senzaki includes relevant precursors in the explicit text of examples processes—including for dependent claim 10. Buchanan does not include in the text of its Example 3 explicit recitation of the metal alkylamide. Second, while Buchanan is focused on the formation of metal, metal oxide, metal nitride or metal silicide films, Senzaki discloses a method that may be used to form mixed metal and metalloid oxides, nitrides, alloys, carbides, carbonitrides, oxycarbonitrides, oxycarbides, oxynitrides, sulfides and other types of films. Ex.1005, Senzaki, 4:47-59. Third, Buchanan discloses various dependent claims that Senzaki does not, including claims 5-6 and

[16] This paragraph's explanation of why Ground #1 is non-redundant applies equally to Ground #2, which is also based on Senzaki.

9. Fourth, Senzaki does not disclose hafnium-based precursors, which are the subject of certain challenged claims (claims 3-4 and 6), while Buchanan and Vaartstra do. Fifth, Senzaki discloses an ALD method while Vaartstra discloses only CVD.

10.1. Claim 1 is obvious over Senzaki in view of Min

10.1.1. [1.P] "A process for making an insulator in a microelectronic device, the process comprising:"

To the extent the preamble is limiting, the combination of Senzaki and Min discloses this limitation. Senzaki states that his invention overcomes the deficiencies in the prior art in forming interlayer dielectrics and gate oxides, both of which are insulators in microelectronic devices. Ex.1005, Senzaki, 2:18-29. Senzaki further provides that the films of the invention are designed to serve, for example, as gate dielectrics in integrated circuit device fabrication, which are insulators in microelectronic devices. *Id.*, 3:40-53; Ex.1003, Banerjee Decl., ¶115.

10.1.2. [1.1] "introducing a first reactant component into a deposition chamber;"

The combination of Senzaki and Min discloses this limitation. Senzaki describes a process in which the vapor of one mixture that includes a metal alkylamide (tetrakis(diethylamido) zirconium, or $Zr(NEt_2)_4$) (first reactant component) is introduced into a "reactor chamber," which is a deposition chamber. Ex.1005, Senzaki, 5:10-26. Senzaki also discloses that its processes can be performed using ALD, whereby "an approximately single layer of precursor

molecules are adsorbed on a surface." *Id.*, 4:4-15. Senzaki thus discloses introducing the vapor of this first mixture into a deposition chamber. Ex.1003, Banerjee Decl., ¶¶116-117.

10.1.3. [1.2] "introducing a second reactant component into the deposition chamber;"

The combination of Senzaki and Min discloses this limitation. Senzaki describes a process in which a second vapor, such as oxygen (second reactant component), is introduced into a "reactor chamber," which is a deposition chamber. Ex.1005, Senzaki, 5:10-26. Senzaki also discloses that its processes can be performed using ALD, whereby "[a] second reactant is dosed onto the first precursor layer followed by a reaction between the second reactant and the first reactant already on the surface." *Id.*, 4:4-15. When forming an oxide, this "second reactant" may be "a source of oxygen . . . selected from the group consisting of oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, air and mixtures thereof." *Id.*, 4:32-37. Senzaki thus discloses introducing a second reactant component (a source of oxygen) into a deposition chamber. Ex.1003, Banerjee Decl., ¶¶118-119.

10.1.4. [1.3] "and alternately repeating introducing the first reactant component and the second reactant component into the deposition chamber;"

The combination of Senzaki and Min discloses this limitation. Senzaki states that its processes can be performed using ALD, whereby the molecules of a

first reactant component are adsorbed onto a surface to form a layer, a second reactant component is then dosed onto, and reacts with, the first precursor layer, and "[t]his alternating procedure is repeated to provide the desired thickness of element or compound in a near atomic thickness layer." Ex.1005, Senzaki, 4:4-15; Ex.1003, Banerjee Decl., ¶120.

10.1.5. [1.4] "wherein deposition of the first reactant component and the second reactant component are self-limiting;"

The combination of Senzaki and Min discloses this limitation. Senzaki discloses that its processes can be performed using ALD and that, when the first reactant component is introduced into the deposition chamber, "an approximately single layer of precursor molecules are adsorbed on a surface." Ex.1005, Senzaki, 4:4-15. A person having ordinary skill in the art would have understood this to mean that Senzaki's deposition processes are or can be made to be self-limiting. Ex.1003, Banerjee Decl., ¶121.

To the extent that Senzaki does not expressly disclose "self-limiting" depositions, it would have been obvious in view of Min. Min discloses that self-limiting deposition is a "distinct characteristic" that can be provided in ALD processes. Ex.1006, Min, p.7 (right), p.9 (left); Ex.1003, Banerjee Decl., ¶121. This is what enables the "single layer" growth to which Senzaki refers, and a person having ordinary skill would have been motivated to ensure that Senzaki's

deposition of reactants is self-limiting to achieve the benefits of ALD, including precise and accurate thickness control, film conformity, and "single layer growth." *See infra* Section 10.5 (motivations to combine Senzaki and Min); Ex.1003, Banerjee Decl., ¶121.

10.1.6. [1.5] "wherein said first reactant component comprises a metal alkylamide;"

The combination of Senzaki and Min discloses this limitation. Senzaki describes using a first precursor mixture (first reactant component) that includes $Zr(NEt_2)_4$, (tetrakis(diethylamido) zirconium). Ex.1005, Senzaki, 3:40-44, 4:4-15, 5:11-42. Tetrakis(diethylamido) zirconium is a metal alkylamide. Ex.1003, Banerjee Decl., ¶122.

10.1.7. [1.6] "wherein said second reactant component interacts with the deposited first reactant component to form the insulator; and"

The combination of Senzaki and Min discloses this limitation. Senzaki describes a process that reacts the deposited first component, which includes a metal alkylamide, with a second reactant component, such as oxygen, to form a metal-metalloid oxide layer. Ex.1005, Senzaki, 3:40-53, 4:32-37, 5:11-42. Senzaki states that its processes can be performed using ALD, whereby the molecules of a first reactant component are adsorbed onto a surface to form a layer, a second reactant component is then dosed onto, and reacts with, the first precursor layer, and "[t]his alternating procedure is repeated to provide the desired thickness of

element or compound in a near atomic thickness layer." *Id.*, 4:4-15. More generally, it was well known in the art that ALD works by having the second reactant react with the deposited first reactant. Ex.1006, Min, p.10 (right) ("When NH_3 is introduced into the reactor, some NH_3 reacts with the TEMAT chemisorbed on surfaces resulting in the formation of TiN films . . . ."); *see also* Ex.1008, Leskelä I, p.17; Ex.1003, Banerjee Decl., ¶124. Senzaki describes that the resulting deposited metal/metalloid oxide layer can be a gate dielectric film, which is an insulator. Ex.1005, Senzaki, 3:40-53; Ex.1003, Banerjee Decl., ¶125.

10.1.8. [1.7] "wherein said insulator comprises oxygen and the metal from the metal alkylamide."

The combination of Senzaki and Min discloses this limitation. Senzaki describes a process that reacts the deposited first component, which includes a metal alkylamide, with a second reactant component, such as oxygen, to form a metal-metalloid oxide layer. Ex.1005, Senzaki, 3:40-53, 4:32-37, 5:11-42. Senzaki describes the resulting layer as "Zr—Si—O," which means that it includes the metal (zirconium, or Zr) from the first reactant component and oxygen (O) from the second reactant component. *Id.*, 3:40-42, 5:13-14; Ex.1003, Banerjee Decl., ¶126. Senzaki further teaches that the resulting Zr-Si-O film is a gate dielectric film, which is an insulator. Ex.1005, Senzaki, 3:40-50.

10.2. Claim 2 is obvious over Senzaki in view of Min

10.2.1. [2] "The process as in claim 1, wherein the insulator insulates a gate or a capacitor."

The combination of Senzaki and Min discloses this limitation. Senzaki describes using ALD to form a metal-metalloid film for use as a "gate dielectric" in "IC [integrated circuit] fabrication." Ex.1005, Senzaki, 3:40-53, 4:4-15, 5:11-42. Senzaki's film therefore "insulates a gate." Ex.1003, Banerjee Decl., ¶127.

10.3. Claim 7 is obvious over Senzaki in view of Min

10.3.1. [7] "A process as in claim 2, wherein the metal alkylamide is a zirconium dialkylamide."

The combination of Senzaki and Min discloses this limitation. Senzaki teaches using a first reactant component that includes $Zr(NEt_2)_4$, (tetrakis(diethylamido) zirconium). Ex.1005, Senzaki, 3:40-44, 5:11-44. Tetrakis(diethylamido) zirconium is a zirconium dialkylamide. Ex.1003, Banerjee Decl., ¶128.

10.4. Claim 10 is obvious over Senzaki in view of Min

10.4.1. [10] "A process as in claim 7, wherein the zirconium dialkylamide is tetrakis(diethylamido) zirconium."

The combination of Senzaki and Min discloses this limitation. Senzaki teaches using a first reactant component that includes $Zr(NEt_2)_4$, (tetrakis(diethylamido) zirconium). Ex.1005, Senzaki, 3:40-44, 5:11-44; Ex.1003, Banerjee Decl., ¶129.

10.5. Motivations to Combine Senzaki with Min

Senzaki describes an ALD process for making a gate insulator (a dielectric material) in a microelectronic device, which process comprises introducing a first reactant component into a deposition chamber, then introducing a second reactant component into the deposition chamber, and alternately repeating introducing the first and second reactant components into the deposition chamber. Senzaki's process further teaches that the first reactant component comprises a metal alkylamide, that the second reactant component comprises oxygen, and that the gate insulator comprises oxygen and the metal from the metal alkylamide.

While Senzaki arguably does not explicitly state that the deposition of the first reactant component and the second reactant component are self-limiting (as claim 1 requires), as set forth below, a person of ordinary skill in the art would have been motivated to combine Senzaki with the teachings of Min to perform an ALD process as described in Senzaki that achieves self-limiting deposition of a first reactant and a second reactant, as described in Min. *See* Ex.1003, Banerjee Decl., Section IX.A.5. Further, a person having ordinary skill would have been motivated to perform ALD using hafnium dialkylamide precursors (as claim 3 requires), in place of zirconium dialkylamide precursors as taught in Senzaki, using self-limiting deposition processes, as taught in Min. Each is addressed in turn.

Senzaki teaches that in the invention it describes, "the above precursors could be used for . . . atomic layer deposition." Ex.1005, Senzaki, 4:4-9. Senzaki further teaches that ALD "provide[s] the desired thickness of element or compound in a near atomic thickness layer" and that "an approximately single layer of precursor molecules are adsorbed on a surface." *Id.*, 4:4-15. One of ordinary skill in the art would have understood this to mean that Senzaki's ALD processes are, or could be made to be, self-limiting, so as to achieve atomic layer growth. Ex.1003, Banerjee Decl., ¶131. This is because self-limiting deposition of reactants is what enables the controlled growth of monolayers of precise thickness. *See id.* at ¶¶44-46, 131*; see also* Ex.1006, Min, pp.9-10, 12.

To the extent that Senzaki does not expressly disclose "self-limiting" processes, however, it would have been obvious to employ "self-limiting" deposition processes to achieve the improved film qualities that self-limited film growth provides.

One of Senzaki's express goals is to use ALD to achieve films of "the desired thickness." Ex.1005, Senzaki, 4:13-15. Senzaki also teaches that such controlled growth is more achievable the closer each ALD cycle gets to providing atomic layer growth. *Id*., 4:4-15. Min teaches that self-limiting deposition processes are a "distinct characteristic of ALD process." Ex.1006, Min, p.9 (left). Min further teaches that it is this characteristic of the ALD process that yields

precise control of film thickness (where film thickness may be controlled by the number of ALD cycles performed) and conformality. *Id.*, pp.10 (left), 12 (left). The benefits of self-limited ALD growth as taught by Min are the same as the express goals taught by Senzaki. Senzaki's references to "desired thickness of element or compound in a near atomic thickness layer" reflect its goal to precisely control the thickness and uniformity of a gate dielectric layer. Ex.1003, Banerjee Decl., ¶133. A person having ordinary skill in the art would have been motivated to employ Min's self-limiting ALD methods to precisely control the thickness of the gate dielectrics in Senzaki via Min's self-limiting growth techniques. *Id.* Indeed, there was industry demand to precisely control the thickness and uniformity of gate dielectrics. *See, e.g., supra* Section 4.3. Accordingly, a person having ordinary skill in the art would have been motivated to implement Min's self-limiting teachings to achieve the goals of Senzaki and precisely control the thickness and uniformity of gate dielectrics.

Employing self-limiting reactant depositions in Senzaki would have been understood to yield predictable results and would have been routine to implement, e.g., simply adjusting the process conditions to achieve self-limiting ALD as taught by Min. Ex.1006, Min, pp.8-9 (describing optimization of vapor deposition process using a metal alkylamide precursor; "it is shown that the transition temperature from ALD to MOCVD is around 230°C".); *see also* Ex.1008, Leskelä

I, p.17 (describing an "ALE window"); Ex.1003, Banerjee Decl., ¶¶44, 134. In fact, Min teaches that the metal dialkylamide precursors of Senzaki would be suitable for self-limiting ALD as taught by Min. Senzaki teaches examples of deposition processes that form Zr-Si-O or Zr-Si-N films using a transition metal precursor -- $Zr(NEt_2)_4$ (tetrakis(diethylamido) zirconium). Ex.1005, Senzaki, 5:11-58. Min uses a transition metal dialkylamide precursor, tetrakis(ethylmethylamido) zirconium (TEMAT), in a self-limiting ALD process. Ex.1006, Min, p.7. Further, other prior art similarly teaches that metal dialkylamides, such as tetrakis(diethylamido) zirconium as taught in Senzaki and tetrakis(ethylmethylamido) titanium as taught in Min, possess such characteristics as stability, volatility, and reactivity. Ex.1003, Banerjee Decl., ¶¶62-63, 134. These characteristics were known to be desirable in ALD precursors for self-limiting processes. Ex.1008, Leskelä I, p.21 (explaining that compounds that are "stable, volatile enough, reactive, cheap and not too difficult to handle" are often good precursors for self-limiting ALD). Thus, one of ordinary skill in the art would have known from the teachings of Min, which are supported by other prior art, that metal dialkylamides, such as tetrakis(diethylamido) zirconium as taught in Senzaki, would be suitable for self-limiting ALD. Ex.1003, Banerjee Decl., ¶134. Further, given Min's teaching of using metal dialkylamides in an ALD process with self-limiting deposition, a person having ordinary skill in the art would have

had a reasonable expectation of success, as Min's teaching of achieving the ALD "window" are directly applicable to Senzaki's ALD process. Ex.1003, Banerjee Decl., ¶¶134-135. One 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; Senzaki teaches that the same precursor may be used to form either a metal oxide or a metal nitride film, with the appropriate choice of second reactant component. *Id.*; Ex.1005, Senzaki, 2:57-59, 4:32-44, 5:11-58. This teaching is supported by other prior art similarly showing that the same precursor could be, and often was, used to form both a metal oxide and a metal nitride film. *See, e.g.*, Ex.1011, George, p.6 (showing in Scheme 1 that $Al(CH_3)_3$ had been used to form both oxide Al_2O_3 (an oxide) and AlN (a nitride); Ex.1008, Leskelä I, pp.21, 25 (describing metal chlorides as having been used as precursors to make both oxide films and nitride films); Ex.1012, Leskelä II, pp.18 ("Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films."), 25-28 (showing a variety of precursors that were used as precursors in ALD processes to form both oxide and nitride film materials); Ex.1013, Bastianini, p.17 (reporting the use of $Zr(NEt_2)_4$, "which had already been successfully employed in the CVD growth of Zr_3N_4 [a nitride] in the presence of NH_3" for deposition of ZrO_2 (an oxide)). Moreover, one of ordinary skill seeking to form a metal oxide would have been motivated to look to Min's ALD process

for forming TiN based on the qualitative similarities between TiN and metal oxides. Ex.1003, Banerjee Decl., ¶135.

Finally, for the same reasons as directly above, the combination would have been obvious to try. Ex.1003, Banerjee Decl., ¶136. Min teaches that ALD conditions may be adjusted and optimized in order to achieve self-limiting ALD deposition and achieve steady, predictable growth of approximately one monolayer per ALD cycle. Ex.1006, Min, pp.8-9 (describing adjustment of experimental conditions to determine the transition temperature between ALD and CVD and determine conditions that "suggest realization of a self-limiting process by adsorption of TEMAT"); 10 (calculating film thickness growth per cycle to be approximately one monolayer or "ML"). Such optimization of process conditions to achieve approximately one monolayer per ALD cycle is routine in semiconductor fabrication. Ex.1003, Banerjee Decl., ¶¶44, 136. Min further teaches advantages of monolayer deposition with self-limiting deposition conditions, including accurate and simple thickness control and excellent conformality. Ex.1006, Min, pp.10, 12. Thus, one of ordinary skill in the art would have been motivated to try this combination to achieve the advantages of self-limiting deposition as taught in Min. Ex.1003, Banerjee Decl., ¶136.

Petitioner believes that Harvard may argue, in response to this petition, that objective indicia support a finding of non-obviousness. For example, in the

prosecution of a related application (Appl. No. 11/199,032) that matured into the 848 Patent,[17] Applicant submitted a declaration from the inventor claiming that the invention solved a long felt need and achieved widespread commercial success. *See, e.g.*, Ex.1014, Gordon Declaration. Note that this declaration and the evidence cited therein are not relevant to the 016 Patent because there is no nexus between this evidence and the claims of the 016 Patent. Claim 1 of the 848 Patent, which was at issue in that prosecution, merely covers a precursor—with no restriction on the use thereof except that it is used "in a thin film deposition process." That is, claim 1 of the 848 Patent covers using this precursor with both CVD and ALD processes, unlike the claims of the 016 Patent, which relate to ALD processes. Ex.1015, 848 Patent, 30:4-5. Nearly all the evidence cited and testimony in the declaration relates to general use of the precursor claimed in the 848 Patent without specifying whether that use is in ALD, CVD, or something else. Ex.1014, Gordon Declaration, ¶¶11-23 (Exhibit A recites the need for a particular high-dielectric constant material, not that it be made with ALD; Exhibit B cites a timeline for a high-dielectric constant material, not how it is made; Exhibit C merely mentions use of a precursor, not use in an ALD process; and

[17] The 016 Patent is a continuation to Appl. No. 11/199,032 (the application that matured into the 848 Patent).

Exhibit D merely mentions sales of a precursor, not how it was used). Accordingly, even if true, the use described in the declaration may therefore be in connection with CVD processes and not ALD processes. Ex.1003, Banerjee Decl., ¶137.

Similarly, the evidence cited and testimony in the declaration regarding the alleged "markedly increased study" into the precursor claimed in the 848 Patent relates to general references to the claimed precursor, rather than specific references to use of the claimed precursor in connection with ALD. Ex.1014, Gordon Declaration, ¶¶22-23. And the evidence cited and testimony in the declaration regarding the number of citations to the declarant's publication (Exhibit E) regarding the claimed precursor, which is about ALD, makes no showing of whether the citations are in publications related to ALD or CVD or why the publications even cite the declarant's article. Finally, this evidence ignores that such general interest, if it did exist, was likely driven by shrinking device sizes that the entire industry was well aware of, not one article. *See* Sections 4.3-4.4; *see also* Ex.1003, Banerjee Decl., ¶137.

That this evidence fails to distinguish between general CVD use and ALD use is notable because it was well established that such precursors are equally

useable in CVD applications.[18] Thus, the declaration submitted during prosecution of the 848 Patent does not support a finding of non-obviousness with respect to the 016 Patent.[19] Ex.1003, Banerjee Decl., ¶137.

11. GROUND #2: CLAIM 8 OF THE 016 PATENT IS UNPATENTABLE AS BEING OBVIOUS OVER SENZAKI IN VIEW OF MIN AND SHIN

As described above, the combination of Senzaki and Min renders claims 1-3, 7 and 10 obvious. *See supra* Section 10.

Regarding claim 8, Senzaki does not expressly disclose tetrakis(ethylmethylamino) zirconium, although it does expressly disclose another zirconium dialkylamide, tetrakis(diethylamino) zirconium. Min expressly discloses the use of tetrakis(ethylmethylamino) titanium in an ALD process, but does not describe tetrakis(ethylmethylamino) zirconium.

[18] Note that there are several other issues with this declaration, such as its reliance on unidentified "personal contacts," *id.* ¶6, and omission its failure to disclose that the alleged need was only relatively recent (not long felt) in light of shrinking device sizes, *see* Section 4.3-4.4.

[19] Petitioner's statements regarding a lack of objective indicia of non-obviousness apply equally to Ground #2.

It would have been obvious, however, to one of ordinary skill in the art to combine the teachings of Senzaki, which describes a zirconium dialkylamide, and Min, which describes an ALD process using the –ethylmethylamino version of a transition metal dialkylamide, with the disclosure in Shin, which teaches tetrakis(ethylmethylamino) zirconium as a species of a genus of compounds that has characteristics comparable to the –dimethylamino and –diethylamino versions of transition metal compounds and can neutralize potential problems presented by the -dimethylamino and –diethylamino compounds. *See infra* Section 11.2 (describing motivations to combine).

11.1. Claim 8 is obvious over Senzaki in view of Min and Shin

11.1.1. [8] "A process as in claim 7, wherein the zirconium dialkylamide is tetrakis(ethylmethylamino) zirconium."

The combination of Senzaki, Min and Shin discloses this limitation. Shin discloses compounds having the general formula "$M[N(CH_3)C_2H_5]_X$." Ex.1007, Shin, p.1. Shin further discloses that in this general formula, "M is selected from the metallic elements belonging to the group 3, group 4, and group 5 on the periodic table, and X is an integer between 3-5." *Id.*; *see also id.,* p.2 ("M is selected from the metallic elements belonging to the group 3A, group 4A, group 4B and group 5B on the periodic table, and X is an integer between 3-5"). Shin further discloses that "it is desirable to use those compounds containing the metallic elements . . . belonging to group 4B such as titanium (Ti) and zirconium

(Zr) . . . as a precursor for the deposition of metal nitride thin film . . . ." *Id.*, p.7. Tetrakis(ethylmethylamino) zirconium, which has a chemical formula of $Zr[N(CH_3)C_2H_5]_4$, thus meets the general formula disclosed in Shin. Ex.1003, Banerjee Decl., ¶140. Shin confirms this, describing "Synthesis of $Zr[N(CH_3)C_2H_5]_4$]in which "79.8 g of yellow tetrakise ethyl methyl amino zirconium solution could be obtained." Ex.1007, Shin, pp.8-9. One of ordinary skill in the art would have been motivated to perform Senzaki's ALD process in a self-limiting fashion as taught in Min, using tetrakis(ethylmethylamino) zirconium as taught in Shin in order to use a metal dialkylamide precursor with characteristics comparable to the precursor disclosed in Senzaki, tetrakis(diethylamino) zirconium, but which may neutralize potential problems presented by tetrakis(diethylamino) zirconium as taught in Shin. *See infra* Section 11.2 (describing motivation to combine).

11.2. Motivations to Combine Senzaki, Min and Shin

As detailed above, one of ordinary skill would have been motivated to combine Senzaki and Min to render claim 7, from which claim 8 depends, obvious. *See supra* Sections 10.3, 10.5. One of ordinary skill in the art would further have been motivated to combine Senzaki and Min with Shin; that is, to perform Senzaki's ALD process in a self-limiting fashion as taught in Min using Shin's

tetrakis(ethylmethylamino) zirconium as a metal alkylamide precursor, for a number of reasons.

First, one of ordinary skill would be motivated to perform Senzaki's ALD process in a self-limiting fashion as taught in Min using tetrakis(ethylmethylamino) zirconium as taught in Shin as a precursor because Senzaki teaches that tetrakis(diethylamino) zirconium is an appropriate choice of precursor for forming a zirconium film (which may be an oxide film or a nitride film) by a vapor deposition process, which process may be ALD. Ex.1005, Senzaki, 3:63-4:15, 5:11-57. Tetrakis(diethylamino) zirconium, disclosed in Senzaki, differs from tetrakis(ethylmethylamino) zirconium only with respect to the type of alkyl groups it contains (one ethyl group and one methyl group, rather than two ethyl groups). Ex.1003, Banerjee Decl., ¶142. Furthermore, Shin teaches that an –ethylmethylamino form of a transition metal dialkylamide, for example of a titanium or zirconium dialkylamide, "exhibits the intermediate characteristics of" the –diethylamino form of the same transition metal dialkylamide, and further "incorporate[s] the advantages" of such compounds. Ex.1007, Shin, pp.6-7. Thus, one of ordinary skill would have been motivated to use Shin's tetrakis(ethylmethylamino) zirconium precursor in Senzaki's ALD process because this compound has, as taught in Shin, characteristics that are comparable to the

compound specifically disclosed in Senzaki as an appropriate precursor for ALD of zirconium films (both oxides and nitrides). Ex.1003, Banerjee Decl., ¶142.

Second, one of ordinary skill would be motivated to perform Senzaki's ALD process in a self-limiting fashion as taught in Min using tetrakis(ethylmethylamino) zirconium as taught in Shin as a precursor because Shin teaches that such a compound may "neutralize" shortcomings of its – diethylamino variant. Ex.1007, Shin, p.7. Shin teaches that tetrakis(ethylmethylamino) zirconium not only has characteristics comparable to and includes advantages of tetrakis(diethylamino) zirconium, but also that this compound could yield improved films in a vapor deposition process. *Id*., pp. 7, 11. Thus, one of ordinary skill would be motivated to use tetrakis(ethylmethylamino) zirconium in Senzaki's ALD process in order to reap the benefits described by Shin. Ex.1003, Banerjee Decl., ¶143.

Third, one of ordinary skill would have had a reasonable expectation of success in performing Buchanan's ALD process in a self-limiting fashion as taught in Min using tetrakis(ethylmethylamino) zirconium as taught in Shin as a precursor because Min teaches that one of the precursors specifically described in Shin successfully achieves self-limiting ALD. Min teaches an ALD process using tetrakis(ethylmethylamino) titanium, or "TEMAT." Ex.1006, Min, p.7. TEMAT not only fits the general formula disclosed in Shin, but is specifically described in

Shin as an exemplary form of its disclosed compound. Ex.1007, Shin, p.7. Min describes using this precursor in an ALD process that successfully achieves self-limiting deposition. Ex.1006, Min, p.9 (left). Thus, one of ordinary skill would have had a reasonable expectation of success in using tetrakis(ethylmethylamino) zirconium in an ALD process such as that described in Senzaki to achieve self-limiting deposition as described in Min. Ex.1003, Banerjee Decl., ¶144.

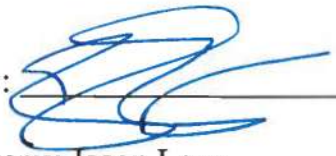
Fourth, it would have been routine for one of ordinary skill to perform Senzaki's ALD process in a self-limiting fashion as taught in Min using tetrakis(ethylmethylamino) zirconium as taught in Shin as a precursor because Min explicitly describes the process of optimizing deposition conditions so as to achieve such self-limiting deposition. *Id.*, ¶145. The optimization process described in Min was further a routine step performed by those in the art in ALD. *Id*. Furthermore, Shin teaches that tetrakis(ethylmethylamino) zirconium "can be made easily" and teaches a method for such preparation. Ex.1007, Shin, pp.7-9. Given these teachings, it would have been routine for one of ordinary skill to perform Senzaki's ALD process in a self-limiting fashion as taught in Min using tetrakis(ethylmethylamino) zirconium as taught in Shin, without the need for undue experimentation. Ex.1003, Banerjee Decl., ¶145.

12. CONCLUSION

For the reasons set forth above, *inter partes* review of claims 1-2, 7-8, and 10 of the 016 Patent is requested.

Respectfully submitted,

Dated: January 12, 2017

By: 

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CERTIFICATE OF COMPLIANCE

1. The undersigned certifies that this brief complies with the type volume limitations of 37 CFR § 42.24(a)(1)(i). This brief contains 10,426 words (excluding the table of contents, the table of authorities, mandatory notices under 37 CFR § 42.8, the certificate of service, certificate of compliance, and appendix of exhibits), as calculated by the "Word Count" feature of Microsoft Word 2010, the word processing program used to create it.

2. The undersigned further certifies that this brief complies with the typeface requirements of 37 CFR § 42.6(a)(2)(ii) and typestyle requirements of 37 CFR § 42.6(a)(2)(iii). This brief has been prepared in a proportionally spaced typeface using Microsoft Word 2010 in Times New Roman 14 point font.

Dated: January 12, 2017

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CERTIFICATE OF SERVICE

The undersigned certifies, in accordance with 37 C.F.R. § 42.105 and § 42.6(e), that service was made on the Patent Owner as detailed below.

Date of service	January 12, 2017
Manner of service	EXPRESS MAIL
Documents served	Petition for *Inter Partes* Review of U.S. Pat. No. 8,334,016 with Micron's Exhibit List Power of Attorney Exhibits Ex.1001 through Ex.1059
Persons served	Patent Owner's Address of Record: WilmerHale 60 State Street Boston, MA 02109 Additional Addresses Known as Likely to Effect Service: William Belanger Alison McCarthy Gregory D. Len Maia H. Harris Griffin Mesmer Pepper Hamilton LLP 19th Floor, High Street Tower 125 High Street Boston, MA 02110-2736

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