

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

**Declaration of Sanjay Banerjee, Ph.D. in Support of
Petition for *Inter Partes* Review
of U.S. Patent No. 8,334,016**

TABLE OF CONTENTS

	Page
I. INTRODUCTION AND QUALIFICATIONS	1
II. MATERIALS RELIED ON IN FORMING MY OPINION.....	5
III. UNDERSTANDING OF THE GOVERNING LAW	6
A. Anticipation	6
B. Invalidity by Obviousness.....	7
IV. LEVEL OF ORDINARY SKILL IN THE ART	8
V. OVERVIEW OF THE TECHNOLOGY AND THE 016 PATENT.....	10
A. Technology Background	11
1. Chemical Vapor Deposition Processes	12
2. Atomic Layer Deposition Processes	18
3. ALD to Deposit Films to Replace Silicon Dioxide as a Gate or Capacitor Dielectric	31
B. The 016 Patent.....	37
VI. 016 PATENT PROSECUTION HISTORY	40
VII. CLAIM CONSTRUCTIONS	46
A. Legal Standard.....	46
VIII. THE PRIOR ART	47
A. U.S. Patent No. 6,537,613 (“Senzaki”).....	47
B. Jae-Sik Min, et al., Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethyldamino)-Titanium and Ammonia (“Min”)	50
C. KR0156980 (“Shin”).....	52
IX. OPINIONS RELATING TO EACH OF THE GROUNDS	54
A. Ground 1: Claims 1-2, 7, and 10 Are Rendered Obvious By Senzaki in View of Min	54
1. Claim 1	55
2. Claim 2	60

3.	Claim 7	61
4.	Claim 10	61
5.	Motivation to Combine Senzaki and Min.....	62
B.	Ground 2: Claim 8 Is Rendered Obvious By Senzaki in View of Min and Shin	70
1.	Claim 8	70
2.	Motivation to Combine Senzaki, Min and Shin	72
X.	Declaration In Lieu of Oath.....	75

I, Sanjay Banerjee, hereby declare as follows:

I. INTRODUCTION AND QUALIFICATIONS

1. My name is Sanjay Banerjee. I have been retained on behalf of Petitioner Micron Technology, Inc. (“Micron”) to provide this Declaration concerning technical subject matter relevant to the *inter partes* review petition (“Petition”) concerning U.S. Patent No. 8,334,016 (Ex.1001, the “016 Patent”). I reserve the right to supplement this Declaration in response to additional evidence that may come to light.

2. I am over 18 years of age. I have personal knowledge of the facts stated in this Declaration and could testify competently to them if asked to do so.

3. My compensation is not based on the resolution of this matter. My findings are based on my education, experience, and background in the fields discussed below.

4. I currently serve as the Cockrell Family Regents Chair Professor of Electrical and Computer Engineering and Director of the Microelectronics Research Center at the University of Texas at Austin (“UT”). Prior to this position, I was first an Assistant Professor (September 1987-August 1990) and later an Associate Professor (September 1990-August 1993) at UT, before being named a Professor in September 1993. Prior to starting my academic work at UT,

I was a member of the technical staff at Texas Instruments (Corporate R&D) from the time I completed my doctoral studies in 1983 until August 1987.

5. In addition to my academic work at UT, I am also the Director of the South West Academy of Nanoelectronics, one of three centers created by the Semiconductor Research Corporation Nanoelectronics Research Initiative in 2006 to research and develop a replacement for conventional metal oxide semiconductor field effect transistors (“MOSFETs”).

6. I received my Ph.D. in Electrical Engineering from the University of Illinois in 1983. I also received an M.S. in Electrical Engineering from the University of Illinois in 1981. I received a B. Tech. in Electronics from the Indian Institute of Technology at Kharagpur in 1979.

7. As described in my CV (Ex.1004), I have more than 30 years of experience in the field of electrical engineering, including extensive experience in semiconductor development and fabrication including that of Dynamic Random Access Memory (“DRAM”), MOSFETs, and beyond-complementary metal-oxide-semiconductor (“CMOS”) transistors. My work in these fields has resulted in more than thirty United States patents related to methods of forming transistors and DRAM cells.

8. Much of my research and experience has related to methods for depositing films, including chemical vapor deposition and atomic layer deposition.

A number of the sponsored research grants on which I have been a principal or co-investigator have related to vapor deposition methods, including “Optoelectronic Devices by Photo-enhanced Chemical Vapor Deposition” (National Science Foundation Presidential Young Investigator Award, August 1988-July 1993), “RPCVD Epitaxial Silicon and Insulators for Use in 3-D CMOS Integrated Circuits” (Office of Naval Research, September 1987-March 1990), “Atomic Layer Epitaxy of Group IV Semiconductors” (Office of Naval Research, February 1991-August 1996), and “Si and Ge Thin Film CVD, Modeling and Control” (U.S. Department of Defense-Multidisciplinary University Research Initiative, July 1995-July 2000). In addition, I am a named author on over seventy publications relating to chemical vapor deposition and atomic layer deposition between 1984 and the present.

9. I am a Fellow of the Institute of Electrical and Electronics Engineers (“IEEE”), the American Physical Society (“APS”), and the American Association for the Advancement of Science (“AAAS”). I have served on numerous professional and government committees in the electrical engineering field, including chairing multiple IEEE committees, meeting and programs, serving on Elsevier Science’s editorial board, and serving as a member on the International Technology Roadmap for Semiconductors (“ITRS”).

10. I have received numerous other awards recognizing my extensive work in the electrical engineering field, which are described in more detail in my CV. I have taught courses in Semiconductor Physics, Solid State Electronic Devices, and Microelectronic and VLSI Device Fabrication at UT. In addition, I have delivered many courses to industry on Semiconductor Devices and Memory and Semiconductor Processing. As a principal investigator, I have been the advisor to over 80 Doctoral and Masters students.

11. I am the author of several books and invited book chapters covering the area of electronic and semiconductor devices including: High-k Gate Dielectrics, Solid State Electronic Devices (three editions), and Novel 3D CMOS. I have authored or co-authored more than 1,000 papers and presentations in the areas of semiconductor devices and electronics development over the course of my career.

12. I have been the recipient of fifty grants to fund my research from a variety of funding agencies including the National Science Foundation (“NSF”), DARPA, the Department of Energy, Semiconductor Research Corporation, the Department of Defense-Multidisciplinary University Research Initiative, and the Office of Naval Research.

13. I have received numerous awards for my work, including the NSF Presidential Young Investigator Award. The NSF Presidential Young Investigator

Award was¹ a highly competitive honor and grant bestowed annually upon recognized academic leaders in science and engineering.

II. MATERIALS RELIED ON IN FORMING MY OPINION

14. In addition to reviewing the 016 Patent, I also reviewed and considered the prosecution history of the 016 Patent (Ex.1002). I also reviewed the prosecution history of U.S. Pat. No. 6,969,539 (the “539 Patent,” Ex.1020) and portions of the prosecution history of U.S. Pat. No. 7,507,848 (the “848 Patent,” Ex.1015), both of which claim priority to the same provisional patent applications to which the 016 Patent claims priority. I have also reviewed the following prior art references described herein: U.S. Pat. No. 6,537,613, to Senzaki et al., entitled “Process for Metal Metalloid Oxides and Nitrides with Compositional Gradients” (“Senzaki,” Ex.1005); 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 (“Min,” Ex.1006); and KR0156980, entitled “Compound for the Deposition of

¹ The NSF Presidential Young Investigator Award was an award given out by the NSF until 1991, at which time it was replaced with the NSF Young Investigator Awards and Presidential Faculty Fellows Program.

Metal Nitride Thin Film and Deposition Method Thereof” (“Shin,” Ex.1007). I also have considered the background materials and exhibits cited herein.

III. UNDERSTANDING OF THE GOVERNING LAW

15. I understand that a patent claim is invalid if it is anticipated or rendered obvious in view of the prior art. I further understand that claims directed to a genus may be anticipated or rendered obvious by a disclosure in prior art of a single species within the claimed genus.

A. Anticipation

16. I have been informed that a patent claim is invalid as anticipated under 35 U.S.C. § 102 if each and every element of the claim, as properly construed, is found either explicitly or inherently in a single prior art reference.

17. I have been informed that a claim is invalid under 35 U.S.C. § 102(a) if the claimed invention was patented or published anywhere in the world, before the applicant’s invention. I further have been informed that a claim is invalid under 35 U.S.C. § 102(b) if the invention was patented or published anywhere in the world more than one year prior to the effective filing date of the patent application (critical date). I further have been informed that a claim is invalid under 35 U.S.C. § 102(e) if an invention described by that claim was disclosed in a U.S. patent granted on an application for a patent by another that was filed in the U.S. before the date of invention for such a claim.

B. Invalidity by Obviousness

18. I have been informed that a patent claim is invalid as obvious under 35 U.S.C. § 103 if it would have been obvious to a person of ordinary skill in the art at the time of the invention, taking into account (1) the scope and content of the prior art, (2) the differences between the prior art and the claims, (3) the level of ordinary skill in the art, and (4) any so-called “secondary considerations” of non-obviousness, which may include: (i) “long felt need” for the claimed invention, (ii) commercial success attributable to the claimed invention, (iii) unexpected results of the claimed invention, (iv) “copying” of the claimed invention by others, (v) failure of others, (vi) praise by others, (vii) recognition of a problem, and (viii) skepticism of experts. I further understand that it is improper to rely on hindsight in making the obviousness determination. My analysis of the prior art is made from the perspective of one of ordinary skill in the art as of the time the invention was made.

19. I have been informed that a claim can be obvious in light of a single prior art reference or multiple prior art references. I further understand that exemplary rationales that may support a conclusion of obviousness include:

(A) Combining prior art elements according to known methods to yield predictable results;

(B) Simple substitution of one known element for another to obtain predictable results;

(C) Use of known technique to improve similar devices (or methods or products) in the same way;

(D) Applying a known technique to a known device (or method or product) ready for improvement to yield predictable results;

(E) “Obvious to try” – choosing from a finite number of identified, predictable solutions, with a reasonable expectation of success;

(F) Known work in one field of endeavor may prompt variations of it for use in either the same field or a different one based on design incentives or other market forces if the variations are predictable to one of ordinary skill in the art;

(G) Some teaching, suggestion, or motivation in the prior art that would have led one of ordinary skill to modify the prior art reference or to combine prior art reference teachings to arrive at the claimed invention.

IV. LEVEL OF ORDINARY SKILL IN THE ART

20. I understand that factors that may be considered in determining the level of ordinary skill in the art may include: (A) “type of problems encountered in the art;” (B) “prior art solutions to those problems;” (C) “rapidity with which innovations are made;” (D) “sophistication of the technology”; and (E) “educational level of active workers in the field.” I also understand that every

factor may not be present for a given case, and one or more factors may predominate. Here, at the time of the alleged invention of the 016 Patent, the industry was conducting research to find a replacement for silicon dioxide (SiO₂) as the insulating film for various applications (e.g., gate dielectric layer, capacitor dielectric layer), and research arms of companies and research institutes were conducting much of this work. The research was being led by those with considerable skill in the art, typically engineers with doctorate degrees, e.g., Dr. Gordon, Dr. Leskelä, Dr. Buchanan, Dr. Vaartstra, myself, and individuals in my research institute to name a few.² The subject matter of this research was specialized.

21. Accordingly, in my opinion, a person of ordinary skill in the art at the time of the claimed inventions would have had 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

² See Ex.1056 (Dr. Gordon’s LinkedIn Profile), Ex.1057 (Dr. Leskelä’s LinkedIn profile), Ex.1058 (Dr. Buchanan’s LinkedIn profile), Ex.1059 (Dr. Vaartstra’s LinkedIn profile).

individual with an advanced degree in a relevant field would require less experience in developing vapor deposition processes to form thin films.

22. I reserve the right to amend or supplement this declaration if the Board adopts a definition of a person of ordinary skill other than that described above, which may change my conclusion or analysis. But should the Board adopt a higher standard or a slightly lower standard, it would not change my opinion that claims 1-2, 7-8, and 10 are invalid (“claims-at-issue”).

23. My opinion below explains how a person of ordinary skill in the art would have understood the technology described in the references I have identified herein around the 2000 time period, which is the approximate date when the provisional applications listed on the face of the 016 Patent were filed. I was a person of at least ordinary skill in the art in 2000.³

V. OVERVIEW OF THE TECHNOLOGY AND THE 016 PATENT

24. The 016 Patent was filed on March 19, 2009. The 016 Patent issued on December 18, 2012. The 016 Patent claims priority to a provisional patent

³ By using the 2000 time period, I am not conceding that the 016 Patent is entitled to the filing dates of its provisional applications, only that the 016 Patent appears to assert priority to those applications.

application filed on September 28, 2000 and a separate provisional patent application filed on November 29, 2000.

25. The 016 Patent relates generally to processes for making an insulator in a microelectronic device, and thus my description of the background technology and the 016 Patent will focus on methods for making insulators in microelectronic devices.

26. Before discussing the details of the specification of the 016 Patent, I will provide some background on the technology used to fabricate insulators in microelectronic devices using vapor deposition processes.

A. Technology Background

27. The relevant aspects of the 016 Patent relate to vapor deposition processes for forming various types of films, including metal silicates, metal phosphates, and metal oxides. First, I will discuss chemical vapor deposition (“CVD”), an umbrella term for processes used to form solid materials from vapor phase reactants. Then I will discuss a type of CVD that is now commonly known as atomic layer deposition (“ALD”), in which reactants are alternately introduced

into a deposition chamber separate from one another.⁴ Although ALD is a type of CVD, my discussion of CVD focuses on CVD techniques in which reactants are co-introduced into a deposition chamber.

1. Chemical Vapor Deposition Processes

28. CVD is a process that forms a thin solid film on a heated surface through chemical vapor-phase reactions and vapor-surface reactions. Ex.1021, Pierson at pp.17, 25-26. CVD is part of a larger class of vapor deposition processes that include physical vapor deposition processes (e.g., evaporation, sputtering, and molecular beam epitaxy). *Id.* However, CVD differs from these processes in that it uses chemical reactions rather than simply physical deposition processes. *Id.*

29. In CVD, reactants (often called “precursors” as they are the precursors to the desired film) are introduced into a deposition chamber in vaporized gaseous form. *Id.* at pp.26-27. These precursor gases are flowed into a chamber containing a heated substrate (such as a silicon wafer for fabrication of a microelectronic device, a solar cell component, or a light-emitting diode film) on which a film is to

⁴ While I refer to atomic layer deposition and ALD throughout this declaration, the technique underlying ALD has been called by many different names, as I will discuss later. *See infra* ¶43.

be deposited. *Id.* at p.17. In most CVD processes, the precursor gases come into contact with one another and chemically react in the vapor phase, leading to by-products which then react with the heated substrate surface, resulting in a thin film being deposited on the substrate surface. *Id.* at pp.25, 38. The precursors are selected according to what type of film is desired. For instance, if a zirconium oxide film is desired, typically a zirconium-containing compound and an oxidant (such as water, oxygen gas, ozone or another oxygen-containing molecule) are used as precursors.

30. In traditional CVD, all of the precursors for a desired film are introduced into the deposition chamber at the same time, and thus chemical reactions between precursors occur in the gas phase and on the substrate surface in the deposition chamber. Ex.1006, Min at p.7. In CVD, the substrate is often heated to high temperatures. Ex.1021, Pierson at pp.36-37.

31. CVD has been known for over a century. Early examples of CVD to deposit metals date from the 1880s.

32. As stated above, CVD is an umbrella term that encompasses a number of vapor deposition techniques. These techniques include: thermal CVD (in which the chemical reactions are encouraged or started using heat); photo-assisted CVD (in which the chemical reactions are encouraged or started using radiation such as ultraviolet light); plasma-enhanced CVD (in which the chemical reactions are

encouraged or started using electrical energy to create a plasma out of the precursor gases in which at least some of the atoms/molecules in the precursor gas become chemically active ions and radicals); and metal-organic CVD (“MOCVD”) (which utilizes metal-organic compounds as precursors). Ex.1021, Pierson at pp.17-18.

33. Unlike physical vapor deposition processes such as sputtering and evaporation, CVD is not a line-of-sight process and is more useful for depositing conformal, uniform films on substrates that possess features such as trenches or recesses or other complex topography. Ex.1022, Fix at p.6.

34. However, while conventional CVD can be useful for vapor deposition, it also presents distinct problems. For example, CVD often requires high deposition temperatures at which substrates may not be thermally stable. Ex.1021, Pierson at pp.17-18; *see also* Ex.1022, Fix at p.6 (explaining that “temperatures required for these CVD reactions are not compatible with thermally sensitive substrates, such as those used in the processing of semiconductor components (e.g., aluminized silicon chips and amorphous silicon solar cells”).

35. Another problem is that when performing CVD, there is often insufficient control of the uniformity and/or thickness of the deposited film. There are a number of reasons for this. First, control over film thickness during CVD is analog—as long as there is a supply of undeposited reactants available in the

chamber, the deposition process will continue, and the film thickness is thus generally proportional to the growth time, excluding some initial incubation period. Because of this, thickness of the growing film must be controlled by adjusting the concentration of reactants that are introduced into the chamber, the temperature, and the length of time that the deposition reaction is allowed to occur, which does not allow precise control of film thickness. Second, precursor molecules, especially where the precursor is particularly reactive, often react directly at their first point of contact/impact with the growth surface. Ex.1023, Gates at p.6. Surface roughness and uneven topography often result from such reactions. *Id.* Third, there can be a lack of control over gas-phase reactions, which can lead to homogeneous gas-phase nucleation of particles which deposit material on the substrate. Ex.1024, Hampden-Smith at p.5. Depending on the growth pressure (which controls the mean free path of precursors) and temperature (which determines the sticking coefficient on the surface), CVD can lead to poor step coverage (the ratio of thickness of a film along the vertical and horizontal surfaces and corners of the topographic features on the substrate). This affects the quality and uniformity of the deposited film. Ex.1006, Min at p.7; *see also* Ex.1025, Suntola II at p.6 (describing the reliance in CVD on a high reaction threshold between reactants to minimize homogeneous gas-phase reactions which can lead to particulate formation and decrease film thickness uniformity).

36. A particularly important type of CVD precursor is the metal-organic category of compounds. Metal-organic precursors are compounds containing a metal and organic (i.e., carbon-containing) ligands. Ex.1024, Hampden-Smith at p.6. Metal-organic precursors include metal alkoxides, β -diketonato complexes, cyclopentadienyl compounds, silanes, and alkyamides. Ex.1012, Leskelä II at pp.18-21.

37. Work on CVD using metal-organic precursors dates back into the early 1960s. Ex.1021, Pierson at p.65. Before 2000, extensive MOCVD work had been done, using metal-organic precursors to deposit metal-containing films by CVD. *Id.* at pp.74-80; *see also* Ex.1024, Hampden-Smith at pp. 7-8 (listing 30+ metal-organic CVD precursors used by 1995).

38. Before 2000, metal-organic precursors had been used in CVD processes, for example, to form zirconium and hafnium oxide films. Zirconium tetra-tert-butoxide, a metal alkoxide (a metal compound wherein an oxygen atom is bound to a metal atom and to an organic group), was widely used as a precursor in forming zirconium oxide thin films by CVD as early as the 1980s. Ex.1026, Smith at p.10; Ex.1055, Brusasco at p.6. Hafnium tetra-tert-butoxide, a similar metal alkoxide precursor, was used to form hafnium oxide thin films by CVD in the same time frame. Ex.1055, Brusasco at p.6.

39. As another example of metal-organic CVD precursors, metal dialkylamides were widely described in MOCVD processes before 2000. Metal dialkylamides are metal precursors having an $M(NR_2)$ structural unit, in which “M” is a metal, “N” is nitrogen bound to the metal, and “R” is an alkyl organic group. Ex.1009, Vaartstra at 4:54-5:18; Ex.1030, Bradley I at p.8. Before 2000, such compounds were known to be desirable CVD precursors due to their volatility, high reactivity, ease of preparation and handling, and long shelf life. Ex.1030, Bradley I at pp.7-8; Ex.1009, Vaartstra at 5:22-27; Ex.1013, Bastianini at p.17; Ex.1022, Fix at pp.6-7.

40. In 1992, Micron filed a patent application describing the use of a titanium dialkylamide precursor, tetrakis(dimethylamino) titanium, in the CVD of titanium nitride/titanium silicide films. Ex.1027, 518 Patent at Abstract, 2:36-42. CVD using this same precursor, as well as zirconium and hafnium dialkylamide precursors (tetrakis(diethylamino) zirconium and tetrakis(diethylamino) hafnium) to form metal nitride films was described in 1991. Ex.1022, Fix at pp.5, 7. A trio of titanium dialkylamides were described in 1996 as precursors for the formation by CVD of titanium nitride films. Ex.1028, Lee at p.11. Metal dialkylamides were also used to form metal oxides as early as the 1990s. For example, tetrakis(diethylamino) zirconium was known for its use in forming zirconium oxide films by CVD. Ex.1013, Bastianini at p.17; *see also* Ex.1009, Vaartstra at

11:8-10 (describing CVD to form films such as metal oxides), 9:32-36 (describing a metal precursor source mixture that includes tetrakis(dimethylamino) titanium).

2. Atomic Layer Deposition Processes

41. As I described above in the context of CVD, ALD is a type of CVD. ALD modifies the CVD process by introducing each vaporized precursor into a deposition chamber alternately and purging the chamber between the introduction of each precursor, rather than introducing all precursors at the same time into the chamber. *See supra* ¶¶27, 29.

42. The basic ALD technique was developed over forty years ago. ALD was originally developed in the 1970s in Finland, by Suntola and colleagues. Ex.1012, Leskelä II at p.13.

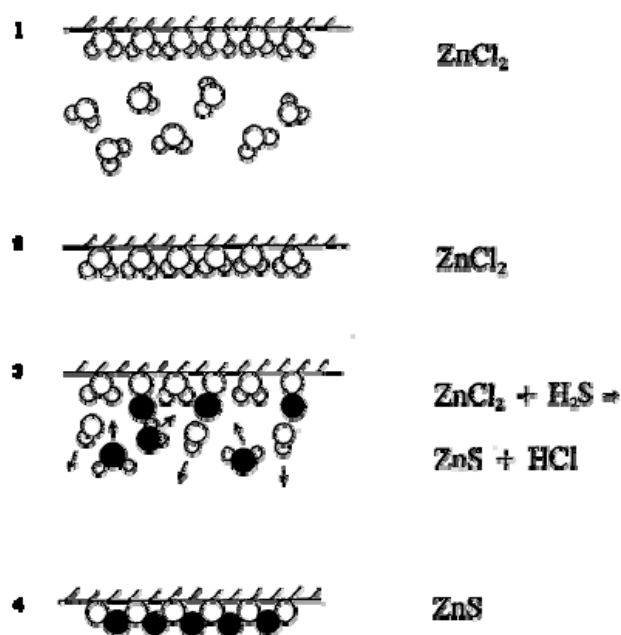
43. Suntola and colleagues originally referred to their invention as “atomic layer epitaxy,” abbreviated as ALE. Ex.1029, Suntola I at p.6. In the beginning, Suntola’s technique was used to deposit single crystalline “epitaxial” films, thus giving rise to the ALE term. Ex.1008, Leskelä I at p.18. However, ALE was also used in the formation of amorphous and polycrystalline films (including metals and metal oxides). *Id.* The use of Suntola’s alternating-precursor method in non-epitaxial applications resulted in a variety of terms being used to describe deposition processes carried out under ALE principles. These terms include: atomic layer deposition, atomic layer processing, chemical vapor

atomic layer deposition, atomic layer growth, successive layer-wise chemisorption, pulsed beam chemical vapor deposition, sequential surface chemical reaction growth, molecular layer epitaxy, binary reaction sequence chemistry, and digital layer epitaxy. *Id.*; Ex.1011, George at p.5. By the late 1990s, “atomic layer deposition” or ALD came to be the popular term for the general principles of Suntola’s ALE method. Ex.1006, Min at p.7; Ex.1012, Leskelä II at p.13; Ex.1031, Ritala I at p.4.

44. ALD generally works as follows: Vaporized precursor gases are pulsed into a deposition chamber containing a substrate alternately, one at a time, with an evacuation step between precursor pulses to remove any undeposited free precursor vapor from the chamber (which may be achieved, for example, by vacuum-pumping the chamber or by purging the chamber with an inert gas such as argon). Ex.1008, Leskelä I at p.17. During the alternating pulses, sequential surface reactions occur in which one component of the desired compound thin film at a time forms on the substrate surface. Ex.1029, Suntola I at p.6. By adjusting the deposition conditions, which is a routine optimization process done in ALD, the sequential surface processes can be made to be “self-controlling” or “self-limiting,” meaning that film growth does not continue as a function of time or the availability of precursor gas. *Id.*; *see also* Ex.1008, Leskelä I at p.17 (describing self-controlled processes in the “ALE window”); Ex.1032, STT at p.13 (referring

to the “self-terminating” surface processes that occur during ALD; “[a]fter all reactive bonds have been occupied by the desired material, the material will ‘grow’ no further.”); Ex.1033, Goodman at p.8 (“Given that, any excess incident molecules or atoms impinging on the film do not stick if the substrate temperature T_{gr} is properly chosen”). For example, optimization of temperature is routinely done to determine when a deposition process transitions from ALD to CVD, and vice versa. See, e.g., Ex.1006, Min at pp.8-9.

45. The self-limiting surface deposition processes that can occur during ALD can be illustrated using growth of zinc sulfide film as an exemplary process:



Ex.1008, Leskelä I at p.17.⁵ In the depiction above, zinc chloride (ZnCl_2) is used as a zinc metal precursor, and hydrogen sulfide (H_2S) is used as a sulfur-containing precursor, to form zinc sulfide (ZnS) through ALD. In the first step (shown to the right of 1 in the figure above), of this exemplary ALD process, vaporized ZnCl_2 is pulsed into the deposition chamber. The vaporized ZnCl_2 adsorbs onto the substrate surface, forming a layer of bound ZnCl_2 on the surface. Then in the second step of this process (shown to the right of 2 in the figure above), the excess, unbound ZnCl_2 is purged out of the chamber, leaving only the ZnCl_2 molecules already bound to the surface in a single layer. *Id.* Importantly, because ZnCl_2 is the only reactant that has thus far been introduced into the reaction chamber, under ALD conditions it adsorbs onto the substrate surface in a single layer. In the third step (shown to the right of 3 in the figure above), vaporized H_2S is introduced into the chamber. The H_2S molecules react with the bound ZnCl_2 , causing an exchange reaction in which the chlorine atoms bound to the zinc attached to the substrate surface are exchanged for sulfur atoms, leaving hydrogen chloride (HCl) as a by-product. In the fourth and final step of this process (shown to the right of 4 in the

⁵ The numbers on the left side of this figure do not appear in the original version, taken from Ex.1008, Leskelä I. I have added them here to assist in my explanation of this figure.

figure above), the unreacted H₂S molecules and the HCl by-product molecules are purged out of the chamber, leaving approximately a monolayer of ZnS on the substrate surface. *Id.* This deposition process is referred to as “self-limiting” because it self-terminates, rather than continuing until there is no more free precursor available. In this exemplary ALD process, one complete cycle consists of the following: (1) pulsing in vaporized ZnCl₂ (the first reactant); (2) purging the chamber to remove all remaining unreacted vaporized ZnCl₂; (3) pulsing in vaporized H₂S (the second reactant); (4) purging the chamber to remove all remaining unreacted vaporized H₂S as well as the HCl by-product that results from the deposition reactions. *See also* Ex.1034, Ritala II at p.7. This cycle is repeated in ALD until the desired film thickness is reached.

46. As depicted in the figure above, ALD can result in a monolayer (or fraction thereof) of the desired film being deposited per growth cycle. Ex.1025, Suntola II at p.5; Ex.1008, Leskelä I at p.17; Ex.1011, George at p.5. This is a key difference between ALD and other types of CVD: while other forms of CVD are discussed in terms of growth rate over a period of time when the substrate is exposed to the precursors, film growth when ALD is made to be self-limiting is not time-dependent but rather cycle-dependent. That is, self-limiting ALD growth is discussed in terms of growth per cycle, rather than over a period of time. Ex.1033, Goodman at p.8; Ex.1008, Leskelä I at p.17.

47. Ideally, self-limiting ALD results in a full monolayer of the desired film being deposited during each ALD cycle. However, due to steric hindrance of the adsorbed precursor molecules (in which the adsorbed precursor molecules are large enough to “block” another precursor molecule from binding to the surface very close to the already-adsorbed molecule), often less than a full monolayer results from each ALD cycle. Ex.1008, Leskelä I at p.17; Ex.1025, Suntola II at p.5. It is thus not unusual in ALD that multiple cycles are needed to achieve a full monolayer of the desired film. *See, e.g.*, Ex.1008, Leskelä I at p.17 (explaining that 2-3 ALD cycles are needed to grow a full monolayer of ZnS, while 5-6 ALD cycles are needed to grow a full monolayer of a cadmium sulfide (CaS) film).

48. ALD provides a number of distinct advantages over other forms of CVD that have made it a very popular and widely-used technique to deposit thin films in semiconductor fabrication. Such advantages were well-known before 2000.

49. For example, ALD can provide a high-quality film at low temperatures. Ex.1035, Ritala III at p.9. As I discussed above, the high temperatures sometimes required for CVD can be detrimental to thermally sensitive substrates. *See supra* ¶34. Additionally, some precursors may thermally decompose at the high temperatures used in CVD; because ALD can be conducted at lower temperatures, such thermal decomposition of precursors may be more

easily avoided. *See, e.g.*, Ex.1006, Min at p.9 (describing saturation of film thickness per cycle, thus achieving a self-limiting process, in ALD at a temperature lower than that at which the precursor begins to thermally decompose).

50. As another example, ALD yields precise control and accuracy over the thickness of a deposited thin film, as a result of the ability to make the ALD growth process self-limiting. Ex.1033, Goodman at p.8 (describing the “absolute control of deposit thickness in terms of the number of cycles employed” which results from a self-limiting ALE approach); *see also* Ex.1008, Leskelä I at p.18, Ex.1035, Ritala III at p.9. Such thickness control is further achieved in a straightforward way by calculating the number of needed growth cycles, without the need to perform thickness monitoring throughout the deposition process. Ex.1029, Suntola I at p.8; Ex.1012, Leskelä II at p.13.

51. Another advantage of ALD over other types of CVD is that ALD achieves uniform film growth over large areas. Ex.1029, Suntola I at p.8; Ex.1035, Ritala III at p.9; Ex.1012, Leskelä II at p.13. This feature of ALD is directly related to the self-limited surface reactions that can take place in ALD—as discussed above, when the surface processes taking place in the deposition process are self-limiting, the film growth rate is not dependent on the reaction rate of the precursors at the surface of the substrate. Ex.1029, Suntola I at p.8; Ex.1012, Leskelä II at p.13. Moreover, in ALD, heterogeneous nucleation at the vapor-

substrate interface (the process that occurs when molecules arrange themselves on the substrate surface) only occurs in two dimensions, thus ensuring uniformity of layers in ultra-thin structures. Ex.1029, Suntola I at p.10.

52. Superior conformality and step coverage is another feature of ALD that results from the self-limiting processes that can occur during this type of deposition and the lack of fluctuation in reactant flow. Ex.1008, Leskelä I at p.18; Ex.1035, Ritala III at p.9; Ex.1031, Ritala I at pp.4-5. Indeed, the excellent conformality achieved in ALD was a main motivation for the initial research into ALD. Ex.1025, Suntola II at p.7.

53. Achievement of a stoichiometric film—that is, a film whose elemental composition is in accordance with the desired compound’s molecular formula and the formula’s numerical ratio of elements—is yet another advantage of ALD. Strict control over the stoichiometry of a deposited film is crucial to many applications in semiconductor fabrication, such as the formation of oxide insulating films, at least because it affords chemical and thermal stability as well as oxidation resistance. Ex.1009, Vaartstra at 1:57-64; Ex.1036, Niinistö at p.5. Thus, by the 1990s, a common consideration by those of ordinary skill in the art was whether a deposition process would yield a stoichiometric film.

54. Control over a film’s stoichiometry may be achieved in ALD by regulating the delivery of precursors into a deposition chamber. Ex.1009,

Vaartstra at 1:64-2:4. Such regulation is an inherent part of ALD, which pulses precursors in alternately and separately from one another in order to regulate the surface processes that are taking place. *See, e.g.*, Ex.1029, Suntola I at p.8; Ex.1008, Leskelä I at p.17-18.

55. Well before 2000, ALD was used to deposit many different types of thin films including oxides, nitrides, silicates, phosphates, sulfides, and single-element films. Ex.1012, Leskelä II at pp.25-28. Deposition of oxides was, in fact, one of the first experiments done by ALD when the technique was developed in the 1970s. Ex.1008, Leskelä I at p.21.

56. Further, many types of metal-containing films, in particular transition metal oxides, have been deposited using ALD. *Id.* at p.19. Transition metals are a category of metallic elements found in periods 4 through 7 in the periodic table. Ex.1037, Hampel at p.3. The transition metal category includes tantalum, titanium, zirconium, hafnium, tungsten, cobalt, manganese, yttrium, vanadium, and a host of other metals. *Id.*

57. Many different types of metal precursors have been used to deposit metal-containing films by ALD. Before 2000, it was known in the art that a number of qualities characterize a desirable precursor for ALD. These include reactivity towards nucleophiles (such as water or alcohols), thermal stability against decomposition at ambient temperatures, and volatility with an adequate

window between vaporization temperature and decomposition temperature. Ex.1012, Leskelä II at pp.13-14. In addition, ideally an ALD precursor does not itself etch the growing film or the substrate itself, nor do its by-products. *Id.* at p.14.

58. It was known before 2000 that in many respects there is much more versatility with respect to choosing ALD precursors, compared to CVD precursors. Ex.1036, Niinistö at p.6. For example, precursors for both CVD and ALD need to be volatile so as to facilitate effective transportation into the deposition chamber. Ex.1012, Leskelä II at pp.13-14. However, there is considerably more flexibility in ALD with regard to precursor volatility because the use of solid precursors with a relatively low vapor pressure is feasible in ALD so long as the vapor pressure is high enough to avoid condensation in the delivery tubes or upon contact with the heated substrate. *Id.*; Ex.1035, Ritala III at p.9; Ex.1036, Niinistö at p.6.

59. As another example, reactivity with the growth surface is a useful characteristic in ALD precursors because the process depends upon the precursors reacting with the substrate or growing film surface. Ex.1012, Leskelä II at p.14. However, unlike in CVD, where precursors that react aggressively with each other are undesirable due to potential gas-phase (non-surface) reactions that can lead to homogeneous nucleation, in ALD aggressive (where there is no risk of gas-phase

reactions) reactivity can be a beneficial characteristic of a precursor. Ex.1036, Niinistö at p.6.

60. The types of metal precursors that have been used in ALD applications to form thin films include halides (metals bound to a halogen element, for example chlorine), alkyl compounds (metals bound to an alkyl group, for example a methyl (CH_3) or ethyl (C_2H_5) hydrocarbon group), metal alkoxides (metals bound to oxygen, wherein the oxygen is also bound to an alkyl group), cyclopentadienyl compounds (metals bound to a C_5H_5 ring group), and metal alkylamides (which are described herein, *see infra* ¶¶62-63). Ex.1012, Leskelä II at pp.18-21, 25-28.

61. Before the 016 Patent’s provisional applications were filed in 2000, it was known in the industry that some types of metal precursors had certain characteristics that make them undesirable for use in ALD. For many years, metal halides were used to perform ALD of metal oxide and nitride films. Ex.1008, Leskelä I at p.21; Ex.1036, Niinistö at p.7 (describing in Table 2 processes using various metal halides to form oxide films). However, some metal chloride precursors were known to etch films, which is a significant drawback to their utility. Ex.1008, Leskelä I at p.21. The potential for residual chlorine to be present in the deposited film is also a major problem when using metal chloride precursors in deposition processes. *See, e.g.*, Ex.1006, Min at p.7; Ex.1012,

Leskelä II at p.14; Ex.1027, 518 Patent at 1:51-53. Alkoxides, moreover, pose challenges in achieving an ideal deposition temperature, since alkoxides can decompose at higher temperatures and can easily convert between isomeric forms. Ex.1038, Buchanan at 2:23-58; Ex.1012, Leskelä II at p.19; Ex.1039, Ritala IV at pp.8-15. Metal nitrates, another type of metal precursor, were known to be extremely sensitive to light, air and water and to potentially form undesirable by-products. Ex.1038, Buchanan at 2:23-58; Ex.1040, Colombo at p.7.

62. Before 2000, metal alkylamides were used in ALD applications and exhibit a number of desirable characteristics for an ALD precursor. For example, titanium dialkylamides (which contain a titanium atom bound to a nitrogen atom, where the nitrogen atom is bound to two alkyl groups) were used to grow titanium-silicon-nitride and titanium nitride films. Ex.1006, Min at p.7; Ex.1012, Leskelä II at p.28.

63. The characteristics of metal alkylamides⁶ have been known since as far back as the 1960s. Ex.1027, 518 Patent at 1:61-2:6. At that time, metal

⁶ I note here that in the nomenclature of metal alkylamide precursors, the suffixes “amino” and “amido” are used interchangeably, which is confirmed both in the art and Harvard’s complaint. For example, $\text{Ti}[\text{N}(\text{C}_2\text{H}_5\text{CH}_3)_4]$ may be referred to as tetrakis(ethylmethyldamino) titanium or tetrakis(ethylmethyldamido) titanium.

alkylamides came to attention as examples of metal-organic compounds wherein the metal was bonded to alkylamino groups. Ex.1030, Bradley I at p.7. Early characterizations of zirconium and titanium dialkylamides found them to be volatile, thermally stable and highly reactive. *Id.* at p.8; Ex.1043, Bradley II at p.5. Later characterizations in the 1990s confirmed the thermal stability of zirconium dialkylamides. Ex.1044, Tsyganova at p.6. Further, the volatility of these compounds and their ability to be vaporized was confirmed in the 1990s. Ex.1009, Vaartstra at 4:65-5:12, 5:54-57; Ex.1022, Fix at pp.6-7. Thus, before the provisional applications for the 016 Patent were filed in 2000, one of ordinary skill in the art would have been aware that metal alkylamides exhibit characteristics desirable for ALD.

64. Prior to the filing of the provisional applications to which the 016 Patent claims priority, the same metal precursor frequently was used to form both a metal oxide and a metal nitride film in both ALD and CVD processes. For *Compare* Ex.1006, Min at p.7 *with* Ex.1041, Bouman at p.10; *see also, e.g.,* Ex.1042, Harvard Complaint, Case No. 1:16-cv-11249, ¶35 (referring to “tetrakis(ethyl-methylamino) zirconium” as having an “amido group selected from the group consisting of dialkylamido, disilylamido and (alkyl)(silyl) amido moieties”) (emphasis added).

example, trimethyl aluminum, $\text{Al}(\text{CH}_3)_3$, was used to form both Al_2O_3 (aluminum oxide) and AlN (aluminum nitride). Ex.1011, George at p.6 (describing uses of $\text{Al}(\text{CH}_3)_3$ as a precursor in Scheme 1). As another example, tetrakis(diethylamino) zirconium, a metal dialkylamide, was used to form both Zr_3N_4 (zirconium nitride) and ZrO_2 (zirconium oxide). Ex.1013, Bastianini, p.17 (reporting the use of $\text{Zr}(\text{NEt}_2)_4$, “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)). See also, e.g., Ex.1038, Buchanan at 20:16-24 (describing the use of a “zirconium-containing precursor” and “hafnium-containing precursor” in a process to deposit either a metal oxide or a metal nitride, depending on whether an oxidant or a nitriding reactant is used); Ex.1008, Leskelä I at pp.21, 25 (describing metal chlorides as having been used as precursors to make both oxide films and nitride films); Ex.1012, Leskelä II at pp.18 (“Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films.”), 25-28 (Table 1 showing a variety of precursors that were used as precursors in ALD processes to form both oxide and nitride film materials).

3. ALD to Deposit Films to Replace Silicon Dioxide as a Gate or Capacitor Dielectric

65. Dielectrics are a key component of semiconductor devices. A dielectric material is a solid that displays low electrical conductivity and that can act as an electrical insulator, electrically isolating two components from each other.

Ex.1045, Graf at p.3. For instance, an insulator can be sandwiched between two electrically conducting plates or electrodes, forming a capacitor, which is an electrical device that can store electrical charge if a voltage is applied across the capacitor. An important example in microelectronics is a Metal Oxide Semiconductor Field Effect Transistor (“MOSFET”), in which a capacitor is inherently formed by the structure of the electrodes above the channel of the MOSFET, with a gate dielectric on top of the channel. The gate electrically gates current flow from a source to a drain, across the channel. For a dielectric, the material’s capacitance, or charge storage capacity divided by the voltage applied, is important. The capacitance is proportional to the dielectric constant of the material, abbreviated as “ κ ,” which is an indication of how much electrical charge can be stored in the capacitor electrodes when a given voltage is applied. Ex.1045, Graf at p.4. The capacitance is also inversely proportional to dielectric thickness. For MOSFETs, there is motivation to increase the gate capacitance by increasing κ and reducing the gate dielectric thickness, so that one can induce more charge in the channel, leading to higher current and improved MOSFET performance at a lower gate voltage. However, one also needs to ensure that the dielectric itself does not electrically conduct or leak current as its thickness is reduced.

66. Traditionally, silicon dioxide (“SiO₂”) was the most widely-used dielectric in semiconductor devices, owing to its ability to form insulators with

desirable dielectric properties. Ex.1046, Buchanan II at p.6. Before 2000, though, those in the art had begun to conduct research geared towards finding a material to replace SiO₂ in semiconductor devices.

67. Moore’s Law is an historical observation that predicts market demand for functionality on a semiconductor device. Specifically, Moore’s Law predicts that the number of components on a semiconductor chip will double approximately every eighteen months. Ex.1047, ITRS Roadmap at p.2. Moore’s Law was observed by those in the semiconductor device field to correctly predict the increases that actually occurred in semiconductor functionality between 1970-2000. *Id.*; *see also* Ex.1034, Ritala II at p.7.

68. As a consequence of Moore’s Law and predictions on future increases in semiconductor functionality needs, in 1999, the ITRS, which focused on “near term needs for the next six years, and then assessing the longer term issues in the years beyond 2005,” noted that the scaling of MOSFETs would present serious issues with respect to the gate dielectric. Ex.1047, ITRS Roadmap at pp.1, 3. The ITRS noted that with the thinning of the oxide used as a gate dielectric, under current conditions in which SiO₂ was used, “[f]or such thin oxides, the gate leakage current due to direct tunneling would become unacceptably large.” *Id.* at p.3; *see also* Ex.1048, 553 Patent at 1:55-63 (statement in a 1997 patent application, “[a]s devices have scaled to smaller and smaller dimensions, the gate

dielectric thickness has continued to shrink. Although further scaling of devices is still possible, scaling of the gate dielectric thickness has almost reached its practical limit with the conventional gate dielectric material, silicon dioxide. Further scaling of silicon dioxide gate dielectric thickness will involve a host of problems; extremely thin layers allow for large leakage currents due to direct tunneling through the oxide.”). The “leading projected solution” was the use of “alternate gate dielectrics with higher relative dielectric constant (κ) than silicon dioxide.” Ex.1047, ITRS Roadmap at p.3; *see also* Ex.1049, Burggraaf at p.1 (describing work on “materials with the potential to overcome ITRS limits of scalability related to gate oxides” and researchers “working their way through the periodic table for a replacement”). Dielectrics with a higher κ could provide sufficient capacitance without requiring them to be so thin as to induce too much charge leakage, which was not feasible using SiO₂. *See infra* ¶¶65-66.

69. Before 2000, research had focused on metal oxides during the search for a SiO₂ replacement due to their high dielectric constants, chemical inertness, oxidation resistance, transparency, electrical resistivity, and low conductivity. Ex.1008, Leskelä I at pp.16, 24; Ex.1011, George at p.14; Ex.1050, Hubbard at p.6. Transition metal oxides in particular were known to have high dielectric constants, and were identified as very promising replacements during the 1990s for silicon dioxide used as the dielectric for gates and capacitors. For example, in

publications on dielectrics in gates and capacitors, those in the industry described using high- κ dielectric materials including zirconium oxide and hafnium oxide, formed using ALD, to replace silicon dioxide as a gate dielectric and as a film in devices with “very-high-aspect-ratio features.”⁷ Ex.1032, SST at pp.6-7; *see also*, *e.g.*, Ex.1051, Kukli at p.6; Ex.1052, Fictorie at p.14; Ex.1013, Bastianini at p.17. Indeed, it was stated in 1999 that “significant progress with hafnium oxide (HfO_2), tantalum oxide (Ta_2O_5), and zirconium oxide (ZrO_3)” had already been reported. Ex.1049, Burggraaf at p.1.⁸

70. Others described the formation of zirconium oxide, titanium oxide, hafnium oxide and other metal oxides as gate dielectrics prior to the filing of the provisional patent applications that led to the 016 Patent. *See, e.g.*, Ex.1038, Buchanan at 23:24-24:34, 26:57-66.

⁷ A trench capacitor is a classic example of a device with “very-high-aspect-ratio features,” in my experience.

⁸ I note that this reference indicates that the chemical formula of zirconium oxide is ZrO_3 , which appears to be a typographical error. Zirconium oxide’s chemical formula is ZrO_2 . *See, e.g.*, Ex.1053, Houssa at p.7.

71. Gate tunneling leakage currents have a strong (exponential) dependence on the dielectric material’s thickness; thus, precise and tight control over film thickness was recognized to be necessary so as to precisely control tunneling leakage. Because those in the field recognized that creating films of precisely controlled thickness would be an important factor going forward in semiconductor devices, in order to accommodate the scaling in accordance with Moore’s Law that was predicted, it was recognized that ALD was a particularly attractive deposition technique because it provides precise thickness control and the ability to form extremely thin layers. Ex.1034, Ritala II at p.7 (noting that the characteristics of ALD, including the ability to achieve self-limiting reactions, large-area uniformity and conformality, and control over film thickness “make ALD an important film deposition technique for future microelectronics.”); Ex.1025, Suntola II at p.8 (describing dielectric strength as a “material characteristic” that is “strongly process related and correlates with the bulk density of the thin film and the density of pinholes,” and further describing ALD as a process that can form thin metal oxide films of high dielectric strength over a large area); Ex.1035, Ritala III at pp.10-11 (examining ALD to form high permittivity dielectric thin films, including transition metal oxides, and noting that using ALD for this process allows “a low temperature deposition of novel dielectrics with high

permittivities and low leakage current densities” with large area uniformity and the ability to scale to large area applications).

72. Those using ALD to form metal oxides as potential replacements for silicon dioxide often looked to precursors that had been successfully used in CVD processes to form metal oxides. For example, zirconium chloride, a precursor often used to deposit zirconium oxide films by CVD, was used in ALD processes in the mid-1990s. Ex.1036, Niinistö at p.7; Ex.1054, Kytökiivi at p.5.

B. The 016 Patent

73. The claims of the 016 Patent at issue in this proceeding relate to processes for making an insulator in a microelectronic device.

74. As I explained in detail above, by 2000 (the date to which the 016 Patent claims priority), efforts to identify a replacement for SiO₂ as an insulating gate dielectric in semiconductor devices were underway. *See supra* Section V.A.3.

75. Moreover, as I explained above, it had already been recognized by 2000 that, given the need for precise thickness control over the very thin films that would need to be formed in devices given the scaling down, size-wise, of devices in the future, ALD would be a useful technique to form these very thin films. *See supra* ¶71.

76. Moreover, as I explained above, it had already been recognized by 2000 that methods to deposit metal thin films using metal chlorides as precursors

in ALD led to undesirable side effects, including the incorporation of residual chlorine in the deposited film and etching of the growing film or substrate by chlorine by-products. *See supra* ¶61.

77. The 016 Patent purports to provide a solution to these recognized problems by proposing the use of “chlorine-free precursors for CVD or ALD of metal silicates or oxides.” Ex.1001, 016 Patent at 2:2-3.

78. While the specification of the 016 Patent states that a feature of the alleged invention is that it permits deposition of materials “by a CVD process in which all the reactants may be mixed homogeneously before delivery to the heated surface of the substrate,” *id.* at 2:27-29, all of the claims of the 016 Patent claim a process for making an insulator that requires alternately repeating introduction of a first reactant component and a second reactant component into a deposition chamber, wherein the deposition of the components is self-limiting and the components interact to form the insulator. *Id.* at 30:9-44.

79. The process recited in claims 1-3 and 5-10 of the 016 Patent is clearly reciting ALD. For example, claim 1 of the 016 Patent requires that the following steps occur in the claimed method of forming an insulator:

- “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.”

Id. at 30:11-17. Claim 1 further sets forth that in the claimed process, “said second reactant component interacts with the deposited first reactant component to form the insulator.” *Id.* at 30:22-23. Claim 1 also sets forth that in the claimed process, “deposition of the first reactant component and the second reactant component are self-limiting.” *Id.* at 30:18-19. The 016 Patent’s specification uses nearly identical language to describe ALD:

The process of the invention may also be carried out using atomic layer deposition (ALD). ALD introduces a metered amount of a first reactant component into a deposition chamber having a substrate therein for layer deposition. A thin layer of the first reactant is deposited on the substrate. After a preselected time period, a metered amount of a second reactant component is then introduced into the deposition chamber, which is deposited on and interacts with the already deposited layer of the first reactant component. Alternating layers of first and second reactant components are introduced into the deposition chamber and deposited on the substrate to form a layer of controlled composition and thickness. . . . It has been determined that the surface reactions are self-limiting so that a reproducible layer of predictable composition is deposited.

Id. at 20:56-21:7 (emphasis added). Thus, it is clear that claim 1 and its dependent claims are claiming an ALD process.

80. The 016 Patent further purports to solve the problems caused by use of chlorine-containing precursors in deposition processes by replacing such precursors with metal alkylamides. For example, the 016 Patent suggests that hafnium oxide may be formed by ALD using tetrakis(dimethylamido) hafnium as a metal precursor. *Id.* at 19:26-44. The 016 Patent further lists exemplary metal amides in Table 1, which exemplary metal amides include a number of transition metal dialkylamides including tetrakis(dimethylamido) hafnium ($\text{Hf}(\text{NMe}_2)_4$), tetrakis(diethylamido) hafnium ($\text{Hf}(\text{NEt}_2)_4$), tetrakis(methylethylamido) hafnium ($\text{Hf}(\text{NEtMe})_4$), tetrakis(dimethylamido) zirconium ($\text{Zr}(\text{NMe}_2)_4$), tetrakis(diethylamido) zirconium ($\text{Zr}(\text{NEt}_2)_4$), and tetrakis(ethylmethylethylamido) zirconium ($\text{Zr}(\text{NEtMe})_4$). *Id.* at Table 1. The hafnium and zirconium compounds listed in this paragraph are recited in the 016 Patent’s dependent claims as specific precursors for the claimed process. *Id.* at 30:31-36, 30:39-44.

81. Accordingly, the 016 Patent claims simply recite already known ALD deposition methods to form insulators, by claiming specific metal alkylamides as precursors in the ALD process.

VI. 016 PATENT PROSECUTION HISTORY

82. I have reviewed the prosecution history of the 016 Patent.

83. The application that led to the issuance of the 016 Patent was originally filed with 20 claims. Ex.1002, 016 Patent FH at p.2-3.

84. For reference, and for the claims-at-issue here, originally-filed claims 1-10 correlate with issued claims 1-10 in the same order. Originally-filed claims 11-20 were cancelled during prosecution of the 016 Patent in response to the Patent Office’s requirement that the applicant elect either claims 1-10 (drawn to a method) or claims 11-20 (drawn to a product). *Id.* at p.3.

85. On March 22, 2012, claims 1-10 were rejected as obvious based on Aarik et al (Thin Solid Films article) (Aarik) in view of U.S. Pat. No. 6,159,855 (Vaartstra). The Examiner found that Aarik disclosed an ALD method of growing hafnium dioxide, an insulator in electronic devices, using an inorganic precursor, hafnium chloride, and that Vaartstra disclosed metal amide compounds for use in CVD, which compounds include tetrakis(diethylamido) hafnium, tetrakis(diethylamido) zirconium, and tetrakis(dimethylamido) zirconium.⁹ The Examiner further found that while tetrakis(ethylmethyldamido) hafnium,

⁹ I note here that while the Examiner’s Office Action refers to “Aarik” as teaching the use of various hafnium and zirconium alkylamides, it appears that the Examiner’s reference to Aarik is a typographical error and that he meant to refer to Vaartstra for these disclosures.

tetrakis(dimethylamido) hafnium and tetrakis(ethylmethyldamido) zirconium are not specifically taught in Vaartstra, one skilled in the art would reasonably expect that these compounds could be used to form a hafnium dioxide film (in the case of tetrakis(ethylmethyldamido) hafnium and tetrakis(dimethylamido) hafnium) or zirconium dioxide film (in the case of tetrakis(ethylmethyldamido) zirconium) given Vaartstra’s teaching of using tetrakis(diethylamido) hafnium and tetrakis(diethylamido) zirconium in ALD of these metal oxides. *Id.* at pp.8-11.

86. On March 22, 2012, claims 1-10 were further rejected on the ground of nonstatutory obviousness-type double patenting in view of claims 24-31 of the 539 Patent in view of Vaartstra. The Examiner found that the 539 Patent taught 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, though it did not specifically teach a metal alkylamide.¹⁰ While I believe that the Examiner’s conclusion regarding an

¹⁰ As noted in my discussion above, a metal alkylamide is a compound in which a metal atom is bound to a nitrogen atom, which nitrogen atom is bound to one or more alkyl groups. *See supra* ¶39. A “metal amide having an amido group selected from the group consisting of dialkylamido, disilylamido and (alkyl)(silyl)

alleged lack of teaching in the 539 Patent of a metal alkylamide (*see supra* n. 9) is incorrect, nonetheless the Examiner found that Vaartstra does disclose metal alkylamides and his rejection was made on that basis. *Id.* at pp.12-13.

87. On September 6, 2012, Applicant amended claim 1 of the 016 Patent to include the following limitation: “wherein deposition of the first reactant component and the second reactant component are self-limiting.” Applicant further stated that this amended limitation, along with claim 1’s recitation of “alternately repeating introducing the first reactant component and the second reactant component into the deposition chamber” showed that “claim 1 is directed to an alternating layer deposition (ALD) process.” *Id.* at p.16.

88. Applicant further argued that, on the basis of the amendment to add the “self-limiting” element and the claim’s recitation of “alternately repeating introducing” the first and second reactant components, neither Vaartstra and Aarik nor the 539 Patent and Vaartstra were combinable to achieve the alleged 016 Patent claims because “CVD and ALD entail using precursor compounds that have amido moieties,” as described in claim 24 of the 539 Patent and recited by the Examiner in his rejection, would include a metal alkylamide. Thus I believe the Examiner was mistaken in his finding that the 539 Patent does not specifically teach a metal alkylamide.

particular types of chemical reactivity particularly suited for each of the deposition techniques.” Applicant relied on a 2006 reference (“Jones”) to support its argument that “one of ordinary skill in the art could not predict a priori whether certain precursors useful for CVD can or cannot be utilized in ALD.” *Id.* at pp.17-18.

89. Applicant further argued that Vaartstra does not teach that any of the precursors described in Vaartstra can provide self-limited growth during deposition. Applicant argued that “the mere mention of a precursor as useful in CVD does not necessarily inform one of ordinary skill in the art whether it can be utilized in an ALD process as well.” *Id.* at p.18. It appears that the Examiner was not aware that metal dialkylamide precursors were well known and had already been well-characterized, going back to the 1960s with the work of Bradley and colleagues, or that the characterization of metal dialkylamide precursors showed them to have characteristics desirable for ALD.

90. On October 10, 2012, the Examiner allowed claims 1-10 to issue as amended. The Examiner noted that while it was well known to form a metal oxide by ALD, to utilize a metal alkylamide to form an oxide film by CVD, and to utilize a metal alkylamide to form a titanium-silicon-nitride film by ALD, “the prior art references fail to teach or suggest using alkylamide to form a metal oxide film by ALD.” *Id.* at p.24.

91. The Examiner made no mention in his Reasons for Allowance of the impact of Applicant’s amendment of claim 1 to include a limitation that “deposition of the first reactant component and the second reactant component are self-limiting.” Accordingly, it does not appear that the Examiner gave significant consideration to this limitation.

92. It should be noted that the Examiner’s Notice of Allowance referred to a 1999 publication by Min and colleagues. *Id.* at pp.24-25.¹¹ The 1999 Min publication describes an ALD process to form a titanium-silicon-nitride film using a metal dialkylamide, tetrakis(dimethylamido) titanium. Ex.1010, Min II at p.6. The Examiner found that “the prior art references fail to teach or suggest using alkylamide to form a metal oxide film by ALD,” but acknowledged that it was well-known to utilize metal alkylamides to form a titanium-silicon-nitride film.

¹¹ This Min publication is cited in the Examiner’s Reasons for Allowance as the “Applied Physics Letters article.” *Id.* at pp.24-25. The Min publication cited by the Examiner is distinct from the Min publication I describe herein as part of the grounds for invalidity of the 016 Patent claims. The Min paper relied on by the Examiner formed a titanium-silicon-nitride film by ALD, whereas the Min paper that serves as a ground for invalidity in the petition formed a titanium nitride film by ALD. *See infra* Section VIII.B.

Ex.1002, 016 FH at p.24. As I explain in more detail below, I believe the Examiner was incorrect in his assessment that the art did not teach or suggest using a metal alkylamide to form a metal oxide by ALD.

VII. CLAIM CONSTRUCTIONS

A. Legal Standard

93. I understand that in deciding whether to institute *inter partes* review, “[a] claim in an unexpired patent shall be given its broadest reasonable construction in light of the specification of the patent in which it appears.” 37 C.F.R. § 42.100(b). I further understand that “the broader standard serves to identify ambiguities in the claims that can then be clarified through claim amendments.” Final Rule, 77 Fed. Reg. 48680, 48699 (Aug. 14, 2012).

94. In forming my opinions as set forth in this declaration, I have accorded all claim terms in claims 1-2, 7-8, and 10 in the 016 Patent their broadest reasonable interpretation, as would be understood by a person of ordinary skill in the art at the time of the alleged invention of the alleged invention of the 016 Patent.

VIII. THE PRIOR ART

A. U.S. Patent No. 6,537,613 (“Senzaki”)

95. I understand that Senzaki is prior art to the 016 Patent under 35 U.S.C. § 102(e). The title of Senzaki is “Process for Metal Metalloid Oxides and Nitrides with Compositional Gradients.” Ex.1005, Senzaki at Title.

96. Senzaki describes the deposition of metal-containing films using vapor deposition processes including ALD. *Id.* at Abstract, 4:4-15. Senzaki describes metal-containing films, such as metal silicates, that had been studied during the 1990s as gate dielectrics. *Id.* at 1:41-49. Senzaki further notes that other types of metal-containing films, such as metal oxides, had been studied and formed by those in the art as thin-film dielectrics. *Id.* at 1:66-2:17.

97. Senzaki addresses the purported failure of the prior art to provide a desirable method for controllably producing a mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer. *Id.* at 2:24-28. Senzaki notes that such films are desirable as gate oxides. *Id.* at 2:18-23.

98. Senzaki teaches that appropriate precursors for forming the mixed metal/metalloid oxides “have ligands which can be the same or different and are selected from a group” that includes metal amides. *Id.* at 3:54-62. The metal in the precursors taught in Senzaki is selected “preferably” from “transition metals,”

including “more preferably” titanium, zirconium, and hafnium. *Id.* at 4:63-5:7. To form oxides, Senzaki teaches a number of reactant sources, including oxygen, ozone, nitrous oxide, and water, among others. *Id.* at 4:32-37. Moreover, Senzaki teaches that the same metal/metalloid precursors can be used either to form an oxide or a nitride, depending on the choice of reactant: “Appropriate choice of precursors, in the presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxynitrides.” *Id.* at 3:63-66.

99. Senzaki states that a number of different deposition processes may be used to form mixed metal/metalloid oxide films. These include ALD. *Id.* at 4:4-15. Indeed, Senzaki describes ALD particularly in teaching the various techniques that can be used to deposit mixed metal/metalloid oxides as gate dielectrics. *Id.* (“In atomic layer deposition, an approximately single layer of precursor molecules are adsorbed on a surface. 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. This alternating procedure is repeated to provide the desired thickness of element or compound in a near atomic thickness layer.”).

100. Senzaki further illustrates the formation of mixed metal/metalloid films using a metal dialkylamide precursor. Specifically, Senzaki describes in Example 1 the use of tetrakis(diethylamido) zirconium, $\text{Zr}(\text{NEt}_2)_4$, and oxygen to

form a Zr-Si-O film. *Id.* at 5:11-43. Senzaki further describes in Example 2 using this same precursor and ammonia to form a Zr-Si-N film. *Id.* at 5:44-58. While both Examples 1 and 2 use CVD to deposit metal/metalloid films, Senzaki makes clear that CVD is merely an exemplary process and that other deposition techniques, including ALD, can be used to deposit the films. *Id.* at 4:4-15. Senzaki’s description of Example 1 further confirms that the conditions for carrying out its disclosed ALD process would be sufficient to vaporize a liquid oxidant, such as water. *See, e.g., id.* at 5:18-20 (describing use of an injection system with a vaporization temperature of 110°C, which is sufficient to vaporize a liquid oxidant such as water, which vaporizes at 100°C).

101. Senzaki describes ALD as providing “the desired thickness of element or compound in a near atomic thickness layer.” *Id.* at 4:13-15. Senzaki further describes ALD as resulting in “an approximately single layer of precursor molecules” being adsorbed onto the substrate surface. *Id.* at 4:9-11. These references would have been understood by one of ordinary skill in the art to suggest that Senzaki’s ALD process either does or can achieve self-limiting deposition, because atomic layer growth is a result of a self-limiting deposition process. *See supra* ¶¶45-46.

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

102. I understand that Min is prior art to the 016 Patent under at least 35 U.S.C. § 102(b) because it was published at least by approximately November 18, 1998, which is more than one year before the earliest provisional application to which the 016 Patent claims priority. The title of Min is “Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethyamino)-Titanium and Ammonia.” Ex.1006, Min at Title.

103. Min relates to the deposition of thin metal diffusion barrier films by ALD using tetrakis(ethylmethyamino)-titanium (abbreviated as “TEMAT” in Min) as a metal precursor. *Id.* at p.7 (left).

104. Min acknowledges that use of the metal halide precursor titanium chloride (TiCl₄) by CVD is problematic because it requires deposition temperatures that are too high and because chlorine impurities and the formation of chloride salts cause corrosion. *Id.* Min teaches that tetrakis(dialkylamino) titanium compounds had been used to deposit TiN (titanium nitride) films by CVD, but that this CVD process does not yield good step coverage or conformality, likely as a result of gas-phase reactions that can occur in CVD. *Id.* Thus, Min teaches using the tetrakis(dialkylamino) titanium compound TEMAT, which does not contain

chlorine, to form metal nitride films by ALD, which avoids gas-phase reactions between reactants. *Id.* (right).

105. In the ALD process taught in Min, a substrate is heated to temperatures between 150° C and 400° C. *Id.* TEMAT and ammonia (NH₃) were used as reactants in an ALD process as follows: TEMAT vapor pulse, Ar purge gas pulse, NH₃ gas pulse, Ar purge gas pulse. *Id.* This sequence was repeated until the desired film thickness was obtained, for 150 cycles. *Id.* at pp.7 (right), 8 (left).

106. Min teaches that “[i]t is important to find out the optimal temperature range for TiN ALD, thus, the dependence of growth rates on substrate temperatures is shown in Fig. 3.” *Id.* at p.8 (right). By carrying out this routine optimization process, Min achieved a temperature range in which film thickness per cycle was independent of substrate temperature, between 170° C and 210° C. *Id.* In contrast, Min noted that above 230° C, ALD was not taking place, but rather CVD was taking place because film thickness per cycle above 230° C gradually increased as a function of temperature. *Id.* Min further teaches optimization of the ALD process within that 170° C - 210° C temperature range, to achieve a self-limiting process (a “distinct characteristic of ALD process”) at both 175° C and 200°C. *Id.* at p.9 (left). Through this optimization process, Min achieved reaction conditions confirming “the ideal linear relationship between number of cycles and

film thickness,” indicating that film thickness increase remained constant over a large number of cycles. *Id.* at pp.10 (right), 11 (left). Moreover, through this optimization process Min achieved deposition by ALD at a temperature lower than the temperature at which the TEMAT precursor would thermally decompose. *Id.* at p.9 (left).

107. The films formed through this self-limiting ALD process taught in Min had “completely continuous” film morphology and conformal film coverage. *Id.* at p.11 (right). Moreover, the films formed through this self-limiting ALD process taught in Min were nearly stoichiometric and there was nearly no indication of particles caused by gas phase reactions. *Id.*

C. KR0156980 (“Shin”)

108. I understand that Shin is prior art to the 016 Patent under at least 35 U.S.C. § 102(b) because it was published on January 28, 1997.

109. Shin describes “organometallic compounds” and methods using such compounds “defined by the following general formula . . . $M[N(CH_3)C_2H_5]X$.” Ex.1007, Shin at p.2. In the general formula described by Shin, “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.* at p.1; *see also id.* at 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

describes its disclosed compound as one in which “nitrogen element forms a covalent bond with” the metal element. *Id.* at p.6. Thus, the general formula Shin describes includes a metal dialkylamide having one methyl (CH₃) and one ethyl (C₂H₅) group.

110. Shin further states that for the general formula disclosed, “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.* at p.7. Shin further describes the use of tetrakis(ethylmethyamido) titanium, Ti[N(CH₃)C₂H₅]₄, as an exemplary embodiment of the claimed compound in a vapor deposition process. *Id.* at p.7.

111. Shin further describes methods for synthesizing a number of species of its claimed compound, including tetrakis(ethylmethyamido) titanium (Ti[N(CH₃)C₂H₅]₄) and tetrakis(ethylmethyamido) zirconium (Zr[N(CH₃)C₂H₅]₄). *Id.* at pp.8-9.

112. Shin explains that compounds according to its general formula, for example tetrakis(ethylmethyamido) titanium and tetrakis(ethylmethyamido) zirconium, share comparable qualities to the –dimethyamido and –diethyamido forms of these transition metal dialkylamides. *Id.* at pp.6-7. Shin further explains that compounds according to its general formula, for example tetrakis(ethylmethyamido) titanium and tetrakis(ethylmethyamido) zirconium,

overcome shortcomings of their –dimethylamido and –diethylamido counterpart compounds in vapor deposition processes. *Id.*

IX. OPINIONS RELATING TO EACH OF THE GROUNDS

113. As I explain in detail below, it is my opinion that claims 1-2, 7-8, and 10 of the 016 Patent are invalid on the following grounds.

A. Ground 1: Claims 1-2, 7, and 10 Are Rendered Obvious By Senzaki in View of Min

114. As explained below, it is my opinion that claims 1-2, 7, and 10 are rendered obvious by Senzaki in view of Min under 35 U.S.C. § 103. In my opinion, Senzaki discloses the well-known process of using ALD to form an insulator in a microelectronic device by introducing a first reactant component and a second reactant component alternately into a deposition chamber, wherein said first reactant component is a metal alkylamide and the resulting insulator comprises oxygen and the metal from the metal alkylamide. To the extent that Senzaki is not found to explicitly disclose that the deposition of the first reactant component and the second reactant component in its disclosed ALD process is or can be made to be self-limiting, I have been asked whether it would have been obvious to one of ordinary skill, and whether a person of ordinary skill in the art would have been motivated, to combine Senzaki with Min’s teachings of self-limiting ALD deposition processes. In my opinion, one of ordinary skill in the art would have been motivated to use Senzaki’s metal alkylamide precursor with a

second reactant component (for example, water, ozone, or oxygen) to form an insulator such as a metal oxide by carrying out self-limiting ALD processes as described in Min, in order to achieve the benefits of ALD as taught in Min. See *infra* Section IX.A.5 (motivation to combine).

1. Claim 1

(a) [1.P] “A process for making an insulator in a microelectronic device, the process comprising:”

115. To the extent that the preamble is limiting, it is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki addresses an alleged lack of methods in the prior art for fabricating materials such as interlayer dielectrics and gate oxides. Ex.1005, Senzaki at 2:18-29. Both interlayer dielectrics and gate oxides act as insulators in microelectronic devices. Senzaki teaches that the films formed in its disclosed method are designed to serve as gate dielectrics in integrated circuit device fabrication. *Id.* at 3:40-53.

(b) [1.1] “introducing a first reactant component into a deposition chamber;”

116. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki describes a process in which the vapor of a first reactant component, for example tetrakis(diethylamido) zirconium, is introduced into a “reactor chamber.” Ex.1005, Senzaki at 5:10-26. A “reactor chamber” such as

that described in Senzaki for a vapor deposition process is a type of deposition chamber.

117. Senzaki further teaches that its method may be carried out by ALD, in which “an approximately single layer of precursor molecules are adsorbed on a surface.” *Id.* at 4:4-15. Thus, when the deposition process used is ALD, Senzaki’s tetrakis(diethylamido) zirconium precursor is introduced as a “first reactant component” into the deposition chamber.

(c) [1.2] “introducing a second reactant component into the deposition chamber;”

118. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki describes a process in which the vapor of a second reactant component is introduced into a “reactor chamber.” Ex.1005, Senzaki at 5:10-26. Senzaki teaches that to form an oxide, this second reactant component is a “source of oxygen,” such as “oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, air and mixtures thereof.” *Id.* at 4:32-37. A “reactor chamber” such as that described in Senzaki for a vapor deposition process is a type of deposition chamber.

119. Senzaki further teaches that its method may be carried out by ALD, in which “an approximately single layer of precursor molecules are adsorbed on a surface.” *Id.* at 4:4-15. Thus, when the deposition process used is ALD, Senzaki’s

source of oxygen is introduced as a “second reactant component” into the deposition chamber.

(d) [1.3] “and alternately repeating introducing the first reactant component and the second reactant component into the deposition chamber;”

120. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki teaches that its disclosed process may be carried out by ALD:

In addition to thermal low pressure CVD, the above precursors could be used . . . by atomic layer deposition. In atomic layer deposition, an approximately single layer of precursor molecules are adsorbed on a surface. 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. This alternating procedure is repeated to provide the desired thickness of element or compound in a near atomic thickness layer.

Id. at 4:4-15. Thus, Senzaki discloses alternately repeating introducing the first reactant component and the second reactant component into the deposition chamber.

(e) [1.4] “wherein deposition of the first reactant component and the second reactant component are self-limiting;”

121. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki discloses an ALD process to deposit a metal-containing film, for example a gate oxide, as I describe above. Senzaki does not explicitly state that the deposition of the first reactant component and the second reactant component in its disclosed ALD process are “self-limiting.” However, Senzaki at least suggests that its ALD deposition processes are or can be made to be self-limiting, because it explains that it deposits “an approximately single layer of precursor molecules” and that the resulting film deposition is “near atomic thickness layer.” Ex.1005, Senzaki at 4:8-15. Further, it was well-known before 2000 that a key characteristic of ALD is that the deposition reactions in ALD can be made to be “self-limiting.” Min confirms this to be true. Ex.1006, Min at pp.7 (right), 9 (left). Thus, in my opinion, it would have been obvious to combine Senzaki’s ALD process with the self-limiting ALD teachings of Min to achieve the benefits of a self-limiting ALD process. *See infra* Section IX.A.5 (motivation to combine).

(f) [1.5] “wherein said first reactant component comprises a metal alkylamide;”

122. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki teaches using a first reactant component, tetrakis(diethylamido) zirconium, in an ALD deposition process. Ex.1005, Senzaki at 3:40-42, 4:4-15, 5:11-44. Tetrakis(diethylamido) zirconium is a metal

alkylamide (a compound with a metal, zirconium, bound to a nitrogen atom that is also bound to an alkyl group or groups, in this case two ethyl groups).

(g) [1.6] “wherein said second reactant component interacts with the deposited first reactant component to form the insulator; and”

123. It is my opinion that the combination of Senzaki and Min discloses this limitation. In the ALD process disclosed by Senzaki, after deposition of the first reactant component, which includes a metal alkylamide (*e.g.*, tetrakis(diethylamido) zirconium), “[a] second reactant is dosed onto the first precursor followed by a reaction between the second reactant and the first reactant already on the surface.” *Id.* at 4:9-15. Senzaki teaches that ALD may be used to perform its disclosed processes. *Id.* at 4:4-9.

124. Moreover, the description of ALD in Senzaki is consistent with how ALD was generally understood to be performed; that is, it was generally understood by those of ordinary skill in the art that in ALD, a second reactant component interacts with a deposited first reactant component to form the desired film. *See supra* ¶¶44-45; *see also, e.g.*, Ex.1006, Min at p.10 (right) (“When NH₃ is introduced into the reactor, some NH₃ reacts with the TEMAT chemisorbed on surfaces resulting in the formation of TiN films”); Ex.1008, Leskelä I at p.17.

125. Senzaki addresses an alleged lack of methods in the prior art for fabricating materials such as interlayer dielectrics and gate oxides. Ex.1005,

Senzaki at 2:18-29. Both interlayer dielectrics and gate oxides act as insulators in microelectronic devices. Senzaki teaches that the films formed in the disclosed method are designed to serve as gate dielectrics in integrated circuit device fabrication. *Id.* at 3:40-53.

(h) [1.7] “wherein said insulator comprises oxygen and the metal from the metal alkylamide.”

126. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki describes a process in which the vapor of a metal alkylamide, tetrakis(diethylamido) zirconium, is reacted with another reactant component, namely an oxygen source, to form a metal/metalloid oxide. *Id.* at 3:40-42, 4:32-37; 5:11-44. In Senzaki’s Example 1, a mixture that includes tetrakis(diethylamido) zirconium reacts with oxygen to form Zr-Si-O. *Id.* at 5:11-44. The resulting Zr-Si-O film thus comprises oxygen (“O”) and the metal (“Zr”) from the metal alkylamide. Senzaki teaches that the Zr-Si-O film is a gate dielectric film, which is an insulator. *Id.* at 3:40-50.

2. Claim 2

(a) [2] “The process as in claim 1, wherein the insulator insulates a gate or capacitor.”

127. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki addresses an alleged lack of methods in the prior art for fabricating materials such as interlayer dielectrics and gate oxides. Ex.1005,

Senzaki at 2:18-29. Senzaki teaches that its disclosed Zr-Si-O film may serve as a “gate dielectric” film, which insulates a gate in integrated circuit device fabrication. *Id.* at 3:40-53.

3. Claim 7

(a) [7] “A process as in claim 2, wherein the metal alkylamide is a zirconium dialkylamide.”

128. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki teaches using a first reactant component, tetrakis(diethylamido) zirconium, in an ALD process. Ex.1005, Senzaki at 3:40-43, 4:4-15, 5:11-44. Tetrakis(diethylamido) zirconium is a zirconium dialkylamide (a compound in which zirconium is bound to a nitrogen atom that is also bound to two alkyl groups, in this case two ethyl groups).

4. Claim 10

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

129. It is my opinion that the combination of Senzaki and Min discloses this limitation. Senzaki teaches using a first reactant component, $\text{Zr}(\text{NEt}_2)_4$, in an ALD process. Ex.1005, Senzaki at 3:40-43, 4:4-15, 5:11-44. $\text{Zr}(\text{NEt}_2)_4$ is the chemical formula for tetrakis(diethylamido) zirconium, a zirconium dialkylamide (a compound in which zirconium is bound to a nitrogen atom that is also bound to two alkyl groups, in this case two ethyl groups).

5. Motivation to Combine Senzaki and Min

130. Senzaki explicitly teaches that its process may be carried out by ALD. Ex.1005, Senzaki at 4:4-15. While Senzaki’s description of ALD arguably does not explicitly state that its ALD process is self-limiting, it is my opinion that one of ordinary skill would have been motivated to combine Senzaki with Min’s ALD teachings that include self-limiting depositions.

131. It is my opinion that one of ordinary skill in the art would have been motivated to perform ALD, as taught in Senzaki, in a self-limiting fashion as taught in Min, in order to achieve the goals of ALD as set out in Senzaki and Min. Senzaki discloses that the precursors it teaches “could be used for . . . atomic layer deposition.” Ex.1005, Senzaki at 4:4-9. Senzaki describes ALD as providing “the desired thickness of element or compound in a near atomic thickness layer.” *Id.* at 4:13-15. Senzaki further states that, in its ALD process, “an approximately single layer of precursor molecules” are adsorbed onto the substrate surface. *Id.* at 4:9-11. As I describe above, it was well known before 2000 that a hallmark of self-limiting ALD deposition processes is that they provide atomic layer growth and that only a single layer of precursor molecules are adsorbed onto a substrate surface. *See supra* ¶¶44-46; *see also* Ex.1006, Min at p.9. Thus, one of ordinary skill would have recognized that Senzaki signals that its ALD process either achieves or can be made to achieve self-limiting ALD deposition.

132. I have been asked to opine whether, if the Board finds that Senzaki does not expressly disclose that its ALD process is self-limiting, one of ordinary skill would have been motivated to perform Senzaki’s ALD process in a self-limiting manner, as taught in Min, in order to achieve the precise atomic layer growth as well as other improved film qualities that result from self-limiting ALD. It is my opinion that it would have been obvious for a number of reasons.

133. First, one of ordinary skill would have been motivated to perform Senzaki’s ALD process in a self-limiting manner as taught in Min because both references teach the same goal, namely, precise control of film thickness. As Min teaches, it was known that self-limiting deposition processes are a “distinct characteristic of ALD process.” Ex.1006, Min at p.9 (left). One of ordinary skill also would have understood that the ability to make ALD self-limiting is what allows precise control of film thickness (*i.e.*, film thickness that may be controlled by the number of ALD cycles that are performed). *Id.* at pp.10, 12; *see also supra* ¶¶46, 50. One of ordinary skill also would have recognized that Senzaki’s references to the “desired thickness of element or compound in a near atomic thickness layer” and the deposition of “an approximately single layer of precursor molecules” per ALD cycle sets forth that a goal of Senzaki’s ALD process is to precisely control film thickness of the desired film, such as a high-dielectric constant gate oxide. This goal was shared by those in the art, as there was high

industry demand to form gate dielectrics of precise thickness and uniformity. See *supra* ¶71. Accordingly, one of ordinary skill would have been motivated to perform Senzaki’s ALD method in a self-limiting fashion as taught in Min to precisely control the thickness of a high-dielectric constant gate oxide.

134. Moreover, it would have been routine to perform Senzaki’s ALD process in the self-limiting fashion disclosed in Min and the results would have been understood to be predictable and to have a reasonable expectation of success. As I describe above, it was routine, when performing ALD, to adjust and optimize process conditions so as to achieve self-limiting growth. See *supra* ¶44. Just such an optimization process is taught by Min. Ex.1006, Min at 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 at p.17 (describing an “ALE window”). Min further teaches that deposition conditions for an ALD process using a metal dialkylamide precursor can successfully achieve self-limiting growth, thereby further teaching that metal dialkylamide precursors (of which tetrakis(diethylamido) zirconium, as disclosed in Senzaki, and tetrakis(ethylmethyldamido) titanium, as disclosed in Min, are species) are suitable for self-limiting ALD. Ex.1006, Min at p.7; Ex.1005, Senzaki at 5:11-58. Other prior art similarly teaches that metal dialkylamides, such as tetrakis(diethylamido) zirconium as taught in Senzaki and

tetrakis(ethylmethyamido) titanium as taught in Min, possess such characteristics as stability, volatility, and reactivity, which were known to be desirable in ALD precursors. Ex.1044, Tsyganova at pp.6-7; Ex.1022, Fix at pp.6-7; Ex.1008, Leskelä I at p.21. This understanding by one of ordinary skill in the art would not have been impacted by the fact that Min describes formation of a metal nitride film rather than an insulator such as a metal oxide; indeed, Senzaki makes clear 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:

An oxygen source can be added [to the disclosed metal-ligand and metalloid-ligand complex precursors] to result in a metal-metalloid oxide, or a nitrogen source can be added to result in a metal-metalloid nitride. . . .

The mixture is mixed with a source of oxygen prior to depositing the multiple metal/metalloid compound layer on the substrate to form the metal and metalloid oxide. The source of oxygen can be selected from the group consisting of oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, air and mixtures thereof. Alternatively, the mixture is mixed with a source of nitrogen prior to depositing the multiple metal/metalloid compound layer on the substrate to form the metal and metalloid nitride. The source of nitrogen can be selected from the group consisting of nitrogen,

ammonia, hydrazine, alkylhydrazine, hydrogen azide,
alkylamine and mixtures thereof.

Ex.1005, Senzaki at 2:57-61, 4:32-44; *see also id.* at 5:11-58 (Example 1 using $\text{Zr}(\text{NEt}_2)_4$ and $\text{Si}(\text{NMe}_2)_4$ to form an oxide film with the addition of an oxygen source, and Example 2 using the same two precursors and a nitrogen source to form a nitride film). Other prior art similarly shows that the same precursor could be, and frequently was, used to form both a metal oxide and a metal nitride film. *See, e.g.,* Ex.1011, George at p.6 (showing in Scheme 1 that $\text{Al}(\text{CH}_3)_3$ had been used to form both oxide Al_2O_3 (an oxide) and AlN (a nitride); Ex.1008, Leskelä I at pp.21, 25 (describing metal chlorides as having been used as precursors to make both oxide films and nitride films); Ex.1012, Leskelä II at pp.18 (“Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films.”), 25-28 (Table 1 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 $\text{Zr}(\text{NEt}_2)_4$, “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)).

135. Moreover, one of ordinary skill whose goal was to form an oxide to insulate a gate or capacitor, as described in Senzaki, would have been motivated to look to Min’s ALD methods for forming TiN based on qualitative similarities

between TiN and metal oxides. Specifically, Min teaches ALD using TEMAT and ammonia to form titanium nitride, TiN, for use as a barrier layer. Ex.1006, Min at p.7. Min discusses TiN as a film in ultra-large scale integration (“ULSI”) devices that require conformal step coverage, especially as via hole aspect ratio continues to increase as device dimensions are reduced. *Id.* In both these devices and the microelectronic devices that Senzaki describes, conformality and precise control of film thickness is extremely important because these parameters strongly affect capacitance, resistance, and leakage currents. Moreover, one of ordinary skill would have known that TiN is considered not to be a true metal (conductive) material, but rather a ceramic semiconductor material with some qualitative similarity to metal oxides.¹² Thus, one of ordinary skill reading Min would have

¹² The energy bandgap of a solid material is a parameter whose magnitude plays a role in determining whether a solid material is considered a conductor, semiconductor, or insulator. True conductors such as metals have an energy bandgap of zero electronvolts (eV). TiN is not considered to be a true metal, but rather a semiconductor, because it has an energy bandgap of approximately 3-4 eV. Metal oxides have a higher energy bandgap; for example, hafnium oxide, which is an insulator, has an energy bandgap of approximately 5-6 eV. Thus, in this

been motivated to use its self-limiting ALD process to form an insulator such as metal oxide, as described in Senzaki, due to this qualitative similarity between the films and the need to deposit a metal oxide with the benefits of ALD, such as good conformality and precise control of film thickness.

136. In addition, for the same reasons as above, the combination of Senzaki’s ALD process using a metal dialkylamide and an oxygen source with Min’s self-limiting ALD process would have been obvious to try. Again, Min teaches that ALD conditions may be adjusted and optimized in order to achieve self-limiting ALD deposition and achieve growth of approximately one monolayer per ALD cycle. Ex.1006, Min at 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”). As I describe above, this type of optimization of process conditions to achieve self-limiting growth during ALD is routine in semiconductor fabrication. And given Min’s teachings of further advantages of monolayer growth during self-limiting ALD, such as accurate and

parameter, TiN bears more qualitative resemblance to insulators than to true conductors.

precise thickness control and conformality of films, one of ordinary skill would have been motivated to try performing Senzaki’s ALD process in a self-limiting fashion as taught in Min to achieve these advantages.

137. I have been asked to review a declaration from Dr. Gordon that was submitted during prosecution of the 848 Patent and provide my opinion on whether it provides objective indicia of non-obviousness with respect to the claims of the 016 Patent. *See, e.g.*, Ex.1014, Gordon Declaration. It does not. The claims of the 848 Patent are directed to a particular hafnium-containing precursor, namely, $\text{Hf}(\text{NEtMe})_4$. The claims recite using the precursor both in CVD processes and in ALD processes. Ex.1015, 848 Patent at 30:4-12. Dr. Gordon’s declaration purports to describe the success of the claimed precursor, but it gives no indication that the cited evidence relates exclusively to use of the precursor in ALD processes, as opposed to use of the precursor in CVD processes. Rather, Dr. Gordon’s declaration merely points to the precursor in question being “widely used in semiconductor industry” to prepare high dielectric materials without demonstrating that the use is specific to ALD. Ex.1014, Gordon Declaration at ¶¶15-16. Likewise, Dr. Gordon’s declaration points to companies that are selling the claimed precursor without demonstrating that the sales are exclusively for use in ALD processes as opposed to use in CVD processes. *Id.* ¶¶19-20. Indeed, Exhibit D to Dr. Gordon’s declaration lists the precursor under the heading

“ALD/CVD Precursors.” *Id.* at p. 13. Similarly, Dr. Gordon’s declaration cites an alleged increase in “scientific interest” in the precursor in question, without indicating whether or how much of this increased “scientific interest” relates specifically to use of the precursor in ALD. *Id.* ¶¶22-25.

B. Ground 2: Claim 8 Is Rendered Obvious By Senzaki in View of Min and Shin

138. While Senzaki does not expressly disclose tetrakis(ethylmethylenamino) zirconium, it does expressly disclose another zirconium dialkylamide, tetrakis(diethylamino) zirconium as an appropriate precursor for its ALD process.

139. In my opinion, it would have been obvious for one of ordinary skill to combine Senzaki’s ALD method (which uses a zirconium dialkylamide and an oxygen source) with Min’s self-limiting ALD process and with Shin’s teaching of tetrakis(ethylmethylenamido) zirconium, thereby rendering claim 8 obvious. See *infra* Section IX.B.2 (describing motivation to combine).

1. Claim 8

(a) [8] “The process as in claim 7, wherein the zirconium dialkylamide is tetrakis(ethylmethylenamido) zirconium.”

140. It is my opinion that the combination of Senzaki, Min, and Shin discloses this limitation. Shin teaches and claims precursor compounds of the general formula “M[N(CH₃)C₂H₅]X” for use in vapor deposition processes. Ex.1007, Shin at pp.1-2, 7-11. 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.* at p. 1; *see also id.* at 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 teaches that titanium and zirconium are preferred metals (“M”) in this general formula. *Id.* at p.7 (“[I]t 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”). Tetrakis(ethylmethylamino) zirconium’s chemical formula is $\text{Zr}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$. *Id.* at p.8. Shin expressly describes “Synthesis of $\text{Zr}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$ in which “79.8 g of yellow tetrakis ethyl methyl amino zirconium solution could be obtained.” *Id.* at p.9 (emphasis added). One of ordinary skill in the art would have been motivated to carry out Senzaki’s ALD method using Min’s self-limiting ALD technique and Shin’s tetrakis(ethylmethylamino) zirconium precursor because such a process would use a precursor with characteristics comparable to the zirconium dialkylamide precursor disclosed in Senzaki as an appropriate precursor for its ALD method, but which may “neutralize” potential problems presented by that precursor as taught in Shin. *See infra* Section IX.B.2 (describing motivation to combine).

2. Motivation to Combine Senszaki, Min and Shin

141. As I explained previously, one of ordinary skill would have been motivated to combine Senszaki and Min to render claim 7 obvious. *See supra* Sections IX.A.3, IX.A.5. In my opinion, one of ordinary skill in the art also would have been motivated to combine Senszaki and Min with Shin, to carry out Senszaki’s ALD method using Min’s self-limiting ALD technique and using Shin’s tetrakis(ethylmethylamino) zirconium as a metal alkylamide precursor, for a number of reasons.

142. First, one of ordinary skill would have been motivated to make the combination because Shin teaches that tetrakis(ethylmethylamino) zirconium “exhibits the intermediate characteristics” of the zirconium dialkylamide disclosed in Senszaki. Senszaki discloses tetrakis(diethylamino) zirconium to be an appropriate precursor for its ALD process. Ex.1005, Senszaki at 3:63-4:15, 5:11-57. Tetrakis(ethylmethylamino) zirconium, which is the zirconium dialkylamide disclosed by Shin, differs from Senszaki’s zirconium dialkylamide compound only in regard to the alkyl groups it contains (one ethyl group and one methyl group, instead of two ethyl groups). Furthermore, Shin teaches that the –ethylmethylamino type of a transition metal dialkylamide, such as titanium or zirconium dialkylamide, “exhibits the intermediate characteristics of” the –diethylamino form of the same transition metal dialkylamide, and “incorporate[s]

the advantages” of such compounds. Ex.1007, Shin at pp.6-7; *see also id.* at p.6 (stating that the compounds meeting the desired criteria “should have characteristics at a level comparable” to the –diethylamino and –dimethylamino forms of the same transition metal dialkylamide). One of ordinary skill would have been motivated to use Shin’s tetrakis(ethylmethylamino) zirconium precursor to carry out Senzaki’s ALD method because Shin teaches that tetrakis(ethylmethylamino) zirconium possesses characteristics “comparable” and “intermediate” to the compound Senzaki identifies as an appropriate ALD precursor. In my experience, it was routine for those of ordinary skill in the art, when performing ALD, to test compounds with “comparable” or “intermediate” characteristics to known precursors, to determine whether such “comparable” or “intermediate” compounds would yield such benefits as taught in Shin.

143. Second, one of ordinary skill would have been motivated to make the combination because Shin teaches that tetrakis(ethylmethylamino) zirconium may “neutralize” shortcomings of tetrakis(diethylamino) zirconium, which is Senzaki’s disclosed precursor. *Id.* at p.7. Shin discloses that tetrakis(ethylmethylamino) zirconium could, if used in a vapor deposition process, provide improved films. *Id.* Thus, one of ordinary skill would have been motivated to use Shin’s tetrakis(ethylmethylamino) zirconium precursor to carry out Senzaki’s ALD process in order to achieve the improved films described by Shin.

144. Third, one of ordinary skill would have had a reasonable expectation of success in carrying out the combination because of Min’s disclosure that one of Shin’s precursors can be used in an ALD process that achieves self-limiting deposition. Min’s ALD process uses tetrakis(ethylmethyamino) titanium, or “TEMAT,” as a metal dialkylamide precursor in an ALD process that achieves self-limiting deposition. Ex.1006, Min at pp.7, 9, 11. Shin identifies both tetrakis(ethylmethyamino) titanium and tetrakis(ethylmethyamino) zirconium as exemplary forms of its claimed compound. Ex.1007, Shin at pp.2, 7-9. Because Min confirms that one of Shin’s precursors when used in Min’s ALD process results in self-limiting deposition, one of ordinary skill would have had a reasonable expectation of success in using another related Shin compound, tetrakis(ethylmethyamino) zirconium, to carry out Senzaki’s ALD process using Min’s self-limiting deposition technique.

145. Fourth, it would have been routine for one of ordinary skill to carry out the combination because Min teaches how to optimize deposition conditions to achieve self-limiting deposition. Min’s optimization is a process that, in my experience, was routinely carried out by those of ordinary skill in the art when performing ALD. Shin further teaches that tetrakis(ethylmethyamino) zirconium “can be made easily” and teaches a method for its preparation, and thus one of ordinary skill would have been able to readily obtain this compound. *Id.* at p.7.

Thus it would have been routine for one of ordinary skill to carry out Senzaki’s ALD method to achieve self-limiting deposition as taught in Min using tetrakis(ethylmethylamino) zirconium as a metal alkylamide precursor as taught in Shin and no undue experimentation would have been necessary.

X. DECLARATION IN LIEU OF OATH

146. I declare that all statements made herein on my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,



Sanjay Banerjee, Ph.D.

Date: January 12, 2017