

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

MICRON TECHNOLOGY, INC.
Petitioner

v.

PRESIDENT AND FELLOWS OF HARVARD COLLEGE
Patent Owner

Case No. IPR2017-00663
Case No. IPR2017-00664
Case No. IPR2017-00666
Patent No. 8,334,016

**DECLARATION OF WAYNE L. GLADFELTER, PH.D. IN SUPPORT OF
PATENT OWNER'S PRELIMINARY RESPONSE**

TABLE OF CONTENTS

I.	Introduction.....	1
A.	Engagement	1
B.	Compensation and Prior Testimony.....	1
C.	Qualifications and Professional Experience.....	1
D.	Summary of My Study	3
II.	Relevant Legal Standards	4
A.	Claim Construction.....	4
B.	Anticipation	5
C.	Obviousness.....	5
III.	One Of Ordinary Skill In The Art	7
IV.	Overview Of The Technology And The '016 Patent	8
A.	Technology Background	8
1.	Chemical Vapor Deposition.....	10
2.	Atomic Layer Deposition.....	11
B.	The '016 Patent	22
V.	Opinion On Claim Construction.....	26
VI.	Opinions On IPR2017-00663	26
A.	Grounds Based on Buchanan and Min.....	26
1.	Summary of the Asserted References.....	26
a.	U.S. Patent No. 6,984,591, “Precursor Source Mixtures” (Buchanan)	27
b.	Jae-Sik Min, et al., Atomic Layer Deposition of TiN Films by Alternate Supply of Tetrakis(ethylmethylamino)-Titanium and Ammonia (“Min”)	31
2.	Petitioner’s Proposed Combination of Buchanan and Min Does Not Teach or Render Obvious Claims 1-3, 5-7, and 10.....	33
a.	The Combination of Buchanan and Min Fails to Disclose or Render Obvious a Self-Limiting ALD Process Using a Metal Alkylamide Precursor to Form a Metal Oxide Film.	35

(1)	Buchanan does not disclose or render obvious a self-limiting ALD process using a metal dialkylamide to form a metal oxide film	38
(a)	Buchanan’s “highly preferred” designation would not direct a person of ordinary skill in the art to metal dialkylamides	40
(b)	Buchanan provides no guidance regarding the suitability of its “preferred precursors” for use in a self-limiting ALD process to form a metal oxide film	44
(c)	Buchanan’s Example 3 does not render obvious a self-limiting ALD process using a metal alkylamide to form a metal oxide film.....	48
(2)	Buchanan fails to teach a viable ALD process for each of the vast amount of metal precursors disclosed	55
(a)	Precursor chemistry is unpredictable	56
(b)	Not all precursors disclosed in Buchanan are suitable for both CVD and ALD.....	58
(3)	A person of ordinary skill in the art would have been dissuaded from using metal dialkylamides in an ALD process to form a metal oxide film.....	63
(4)	A person of ordinary skill in the art would not have combined the teachings of Buchanan and Min to arrive at the process of Claim 1	68
b.	The Combination of Buchanan and Min Fails to Disclose or Render Obvious Claims 2-3, 5-7, 9-10 of the ’016 Patent.....	75
(1)	Claim 2: The process as in Claim 1, wherein the insulator insulates a gate or a capacitor.....	75

(2)	Claim 3: The process in Claim 2, wherein the metal alkylamide is a hafnium dialkylamide.	76
(3)	Claim 5: The process as in Claim 3, wherein the hafnium dialkylamide is tetrakis(dimethylamido)hafnium.	77
(4)	Claim 6: A process as in Claim 3, wherein the hafnium dialkylamide is tetrakis(diethylamido)hafnium.	77
(5)	Claim 7: A process as in Claim 2, wherein the metal alkylamide is a zirconium dialkylamide.	78
(6)	Claim 9: A process as in Claim 7, wherein the zirconium dialkylamide is tetrakis(dimethylamido)zirconium.	78
(7)	Claim 10: A process as in Claim 7, wherein the zirconium dialkylamide is tetrakis(diethylamido)zirconium.	79
B.	Grounds Based on Buchanan, Min, and Shin	80
1.	Summary of Korean Patent KR0156980 “Compound for the Deposition of Metal Nitride Thin Film and Deposition Method Thereof” (“Shin”)	80
2.	A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Buchanan, Min, and Shin.....	80
VII.	Opinions On IPR2017-00664	83
A.	Grounds Based On Senzaki and Min	83
1.	Summary of the Asserted References	83
a.	U.S. Patent No. 6,537,613, “Process For Metal Metalloid Oxides And Nitrides with Compositional Gradients” (“Senzaki”)	83
2.	Petitioner’s Proposed Combination of Senzaki and Min Does Not Render Obvious Claims 1, 2, 7, and 10	85
a.	A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Senzaki and Min to Arrive at the Process Recited by Claim 1 of the ’016 Patent.	86
(1)	A person of ordinary skill in the art would see that Senzaki and Min have directly contrary goals.	87

(2)	A person of ordinary skill in the art would not have understood modifying Senzaki's CVD process in view of Min to yield predictable results nor be routine to implement.....	89
(3)	A person of ordinary skill in the art would not have known that certain precursors were "desirable" for ALD processes.....	92
(4)	A person of ordinary skill in the art would have had no reasonable expectation of success modifying Senzaki's CVD process in view of Min.	93
(5)	A person of ordinary skill in the art would not have found it obvious to try modifying Senzaki's CVD process in view of Min.	98
B.	Grounds Based On Senzaki, Min, and Shin.....	99
1.	Petitioner's Proposed Combination of Senzaki, in view of Min, and Shin Do Not Render Obvious Claim 8.....	100
a.	A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Senzaki, Min, and Shin to Arrive at the Process Recited by Claim 8 of the '016 Patent.....	101
(1)	A person of ordinary skill in the art would know that changes in alkyl groups of a precursor could cause non-linear unpredictable effects.	101
(2)	A person of ordinary skill in the art would know that CVD disclosures do not ensure success in an ALD process.....	103
(3)	A person of ordinary skill in the art would not have had a reasonable expectation of success in using tetrakis(ethylmethylamino) zirconium in an ALD process.....	104
(4)	A person of ordinary skill in the art would not have found the proposed combination to be routine.....	105
VIII.	Opinions on IPR2017-00666.....	107
A.	Grounds Based on Vaartstra and Min	107

1.	U.S. Patent No. 6,159,855, “Organometallic Compound Mixtures in Chemical Vapor Deposition” (“Vaartstra”).....	107
2.	Petitioner’s Proposed Combination of Vaartstra and Min Does Not Render Obvious Claim 1	109
a.	A Person of Ordinary Skill in the Art Would Have Had No Expectation of Success Modifying Vaartstra’s CVD Process in View of Min’s ALD Process	111
b.	A Person of Ordinary Skill in the Art Would Not Have Been Motivated to Modify Vaartstra’s Process in Light of Min	115
B.	Grounds Based on Vaartstra, Min, and Ma.....	122
1.	U.S. Patent No. 6,200,866, “Use of silicon germanium and other alloys as the replacement gate for the fabrication of MOSFET” (“Ma”).....	123
2.	Vaartstra, Min, and Ma Do Not Render Obvious Claims 2, 3, 6, 7, 9, and 10.....	123
C.	Grounds Based on Vaartstra, Min, Ma, and Bradley II	123
1.	D.C. Bradley et al., “Metallo-organic Compounds Containing Metal-Nitrogen Bonds. Part VI. Infrared and Nuclear Magnetic Resonance of Dialkylamido-derivatives of Titanium, Vanadium, Zirconium, Niobium, Hafnium, Tantalum, and Thorium” (“Bradley II”).....	124
2.	A Person of Ordinary Skill in the Art Would have no Motivation to Combine the Teachings of Bradley II with Vaartstra, Min, and Ma	124
D.	Grounds Based on Vaartstra, Min, Ma, and Shin	126
1.	Vaartstra, Min, Ma, and Shin Do Not Render Obvious Claim 8	127

I, Wayne L. Gladfelter, Ph.D., do hereby declare:

I. INTRODUCTION

A. Engagement

1. I have been retained by Patent Owner President and Fellows of Harvard College (“Harvard”) to provide expert opinion and testimony on certain issues concerning *Inter Partes* Review Nos. IPR2017-00663, 00664, 00666 of U.S. Patent No. 8,334,016 (hereafter “the ’016 Patent”). This is my declaration in support of Patent Owner’s Preliminary Responses.

B. Compensation and Prior Testimony

2. I am being compensated at a rate of \$570 per hour. My compensation is in no way dependent upon or contingent upon the opinions and testimony that I render during the course of this case.

3. I have never previously testified as an expert.

C. Qualifications and Professional Experience

4. I am currently a professor in the Department of Chemistry at the College of Science and Engineering at the University of Minnesota. I have been a professor in the Department of Chemistry at the College of Science and Engineering at the University of Minnesota since 1988. I have taught, and continue to teach, courses to undergraduate and graduate level students in the areas of general, inorganic, organometallic and materials chemistry. My research at

University of Minnesota is focused in the areas of inorganic and organometallic chemistry in vapor deposition reactions, dye-sensitized nanoparticles, atomic force microscopy of polymers, and the reaction mechanisms involved in chemical vapor deposition and atomic layer deposition.

5. Prior to my current position at University of Minnesota, I was an assistant professor from 1979 to 1984 and an associate professor from 1984 to 1988 in the Department of Chemistry at the University of Minnesota. I taught courses to undergraduate and graduate level students in the areas of general, organic, inorganic, organometallic and materials chemistry. In addition to teaching, I also performed research in the areas of organometallic metal clusters and homogeneous catalysis. Prior to the University of Minnesota, I was a National Science Foundation Postdoctoral Fellow at the California Institute of Technology.

6. I have been a Member of the editorial advisory board for the Journal of Coordination Chemistry (2010-present), Ceramics International (2002-present), Chemical Vapor Deposition (1994-2015), Inorganic Chemistry (2013-2016) and Chemistry of Materials (1990-1996 and 2003-2008). In 2007, I co-organized a symposium at the American Chemical Society meeting on CVD and ALD. I served as the chair of the Department of Chemistry (1999-2005) and associate dean for academic affairs in the College of Science and Engineering (2007-2013) at the University of Minnesota.

7. I have written review articles entitled “Liquid and Solid Precursor Delivery Systems in Gas Phase Processes” (2015), “Chemical Vapor Deposition of Metals: W, Al, Cu and Ru” (2009), “The Use of Aluminum and Gallium Hydrides in Materials Science” (2000), “Chemical Vapor Deposition of Aluminum” (1994), and “Selective Metallization by Chemical Vapor Deposition” (1993).

8. I received my Bachelor of Science degree from the Colorado School of Mines, and my doctorate degree in inorganic and organic chemistry from The Pennsylvania State University. For my doctorate degree, the focus of my studies was in the area of organometallic metal carbonyl cluster compounds. I received my doctorate degree in 1978.

9. A copy of my curriculum vitae is attached as Exhibit A.

D. Summary of My Study

10. I am aware that the IPR2017-00663, -00664, -00666 Petitions for *Inter Partes* Review filed in the above-identified proceedings assert grounds of invalidity of claims of the '016 Patent. IPR2017-00663 Paper 1 (“’663 Petition”), IPR2017-00664 Paper 1 (“’664 Petition”), IPR2017-00666 Paper 1 (“’666 Petition”), (collectively, “the Petitions”)¹.

¹ I note that Petitioner’s exhibits across the Petitions, while similar, do not all share the same exhibit numbers. For ease of reference, unless directly addressing the grounds of a specific petition, I will use the exhibit numbers from the ’663 Petition.

11. I have reviewed the '016 Patent, the Petitions, the Declarations of Dr. Sanjay Banerjee, Ph.D. in support of the Petitions (“’663 Banerjee Decl.”, “’664 Banerjee Decl.”, “’666 Banerjee Decl.”) (collectively “the Banerjee Declarations”), and the references relied upon for Grounds presented in the Petitions.

12. My opinions are set forth below, and are based on my years of education, research, and experience, as well as my investigation and study of the materials identified above. I make these statements based upon facts and matters within my own knowledge or on information provided to me by others. All such facts and matters are true to the best of my knowledge and belief.

II. RELEVANT LEGAL STANDARDS

13. My understanding of the relevant legal standards is based on information provided to me by Patent Owner’s counsel.

A. Claim Construction

14. I understand that in an *inter partes* review proceeding, the claims of a non-expired patent are construed from the perspective of one of ordinary skill in the art at the time of the claimed invention and are given their broadest reasonable construction consistent with the specification.

B. Anticipation

15. I understand that a claim is anticipated if a single prior art reference discloses, explicitly or inherently, all limitations of the invention arranged or combined in the same way as in the claim. I further understand that inherency may not be established by probabilities or possibilities, and the fact that one of ordinary skill in the art understands that the missing limitation could exist under certain circumstances is not sufficient. Instead, the party claiming inherency must prove that the missing limitation is necessarily present and that it would be so recognized by a person of ordinary skill in the relevant art. Whether the inherent disclosure was recognized at the time of the reference is immaterial.

16. I further understand that the disclosure of an anticipatory reference must describe the claimed invention to a degree adequate to enable a person of ordinary skill in the art to not only comprehend the invention, but also to make, or in the case of a method, use, the claimed invention without undue experimentation. Provided that the reference asserted is enabling, it is my understanding that it need not disclose any independent use or utility to anticipate a claimed invention.

C. Obviousness

17. It is my understanding that an invention is unpatentable if the differences between the invention and the prior art are such that the subject matter of the invention as a whole would have been obvious at the time the invention was

made to a person having ordinary skill in the art. I further understand that obviousness is determined by evaluating: (1) the scope and content of the prior art, (2) the differences between the prior art and the claim, (3) the level of ordinary skill in the art, and (4) secondary considerations of nonobviousness. To establish obviousness based on a combination of prior art references, it is my understanding that a petitioner must identify a specific combination that teaches all limitations and establish that a person of ordinary skill in the art at the time of the claimed invention would have found it obvious to make that combination.

18. To guard against hindsight and an unwarranted finding of obviousness, I understand that an important component of any obviousness inquiry is whether the petitioner has identified any teaching, suggestion, or motivation that would have prompted a person of ordinary skill in the art to make the claimed combination and have a reasonable expectation of success in doing so. I understand that this test should not be rigidly applied, but can be an important tool to avoid the use of hindsight in the determination of obviousness.

19. I further understand that the teaching, suggestion, or motivation may be found explicitly or implicitly: (1) in the prior art; (2) in the knowledge of those of ordinary skill in the art that certain references, or disclosures in those references, are of special interest or importance in the field; or (3) from the nature of the problem to be solved. Additionally, I understand that the legal determination of

the motivation to combine references allows recourse to logic, judgment, and common sense. In order to resist the temptation to read into prior art the teachings of the invention in issue, however, it should be apparent that “common sense” should not be conflated with what appears obvious in hindsight.

20. I understand that it is improper to combine references where the references teach away from their combination. I understand that a reference may be said to teach away when a person of ordinary skill in the relevant art, upon reading the reference, would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the applicant. I further understand that if the teachings of a prior art reference would lead a person of ordinary skill in the art to make a modification that would render another prior art device inoperable, then such a modification would generally not be obvious. I also understand that if a proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose, then there would have been no suggestion or motivation to make the proposed modification.

III. ONE OF ORDINARY SKILL IN THE ART

21. I understand that Petitioner and the Banerjee Declarations have alleged that a person of ordinary skill in the art in the field of the invention claimed

in the '016 Patent would be a person with “at least a Bachelor of Science degree in electrical engineering, chemical engineering, chemistry, physics, materials science, or a closely related field, along with at least 5 years of experience in developing vapor deposition processes to form thin films. An individual with an advanced degree in a relevant field would require less experience in developing vapor deposition processes to form thin films.” ’663 Petition at 21, ’664 Petition at 21, ’666 Petition at 21-22; *see also* e.g., ’663 Banerjee Decl. at ¶21.

22. I believe I am qualified based on my education and experience, discussed above, to render opinions from the perspective of a person of ordinary skill in the art according to Petitioner’s proposed definition, and for the purposes of my opinions herein, I have used this definition. In particular, I have read the ’016 Patent, Buchanan, Vaartstra, Senzaki, Min, Shin, Ma, Bradley II and have considered their disclosures from the perspective of such a person of ordinary skill in the art at the time of the invention of the ’016 Patent. Unless otherwise stated, my statements made herein refer to the knowledge of one of ordinary skill in the field of the invention claimed in the ’016 Patent.

IV. OVERVIEW OF THE TECHNOLOGY AND THE ’016 PATENT

A. Technology Background

23. From my review of the ’016 Patent, its prosecution history, as well as various background materials referenced in the patent and the Banerjee

Declarations together with my own lengthy experience with the technology at issue, I will now provide an overview of the technology and a background of the inventions.

24. The inventions of the '016 Patent relate to novel processes and reagents for thin film deposition, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). Ex. 1001 at 1:30-32. Claims 1-3 and 5-10 of the '016 Patent, currently at issue, specifically relate to the use of metal amides in a self-limiting ALD process to produce a metal oxide film. Ex. 1001 at 30:9-26 (Claim 1).

25. The patented inventions relate to the specific processes and materials used in the deposition of thin films on surfaces, such as those deposited in the manufacture of microelectronics. Ex. 1001 at 2:48-52. Each of these deposition methods requires chemical reactions to form thin films on a surface. Ex. 1001 at Abstract, 1:46-2:7. The deposition process chosen to create a thin film generally drives the kind of precursors that are selected to be used with that process, and also results in films with different features. *Id.* at 1:40-2:3, 2:14-61.

26. Generally, CVD is a deposition process for forming solid materials, such as coatings or powders, from reactants in the vapor phase. Ex. 1001 at 1:38-40. In CVD processes, a single reactant vapor or vapor mixture is brought into contact with a heated surface on which a thin film is deposited. Ex. 1001 at 1:46-

48. A CVD process using only one reactant vapor is referred to as “single source CVD.” In a CVD process using more than one reactant vapor, or mixture of reactant vapors, the reactant vapors are exposed to the heated surface simultaneously.

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

1. Chemical Vapor Deposition

28. In a CVD process, reactant vapors are selected that will allow for the continuous growth of a thin film on a heated surface. *See* Ex. 1001 at 1:37-48. As mentioned above, in CVD one or more reactant vapors are introduced into a reaction chamber, also referred to as a deposition chamber, which contains a heated surface, often referred to as a substrate. *See id.* at 1:37-2:3, 2:26-29. This allows a continuous thin film to form on the surface for as long as it is exposed to the reactant vapor. In an example of CVD with two reactant vapors, at least one

reactant vapor must be reactive with the initial surface, and both reactant vapors must be reactive with the deposits formed by the other reactant vapor. *Id.* This allows initial deposits on the surface and for the resulting layer to continue to grow for as long as it is exposed to the reactant vapors. *Id.* In a CVD process, it is also possible for one or more of the reactant vapors to undergo a chemical reaction in the vapor phase prior to reacting with the substrate surface. *Id.*

29. A characteristic of CVD is that thin films can be grown quickly because the growth is continuous. However, the continuous growth in CVD makes it more difficult to control the thickness of the thin film than with ALD. *See* Ex. 1001 at 137-54; *see also, e.g.,* Ex. 1047 at 319; Ex. 1048 at 223. For a desired thickness, the reactant vapors must be removed from the deposition chamber at precisely the right time. Additionally, it is more difficult to control the uniformity (i.e., amount of growth across the surface) of the thin film because locations with more exposure to reactant vapors may have thicker layers and the continuous nature of the reaction can amplify this effect. This becomes a more serious problem when the substrate to be coated has irregularly shaped features on the surface such as trench.

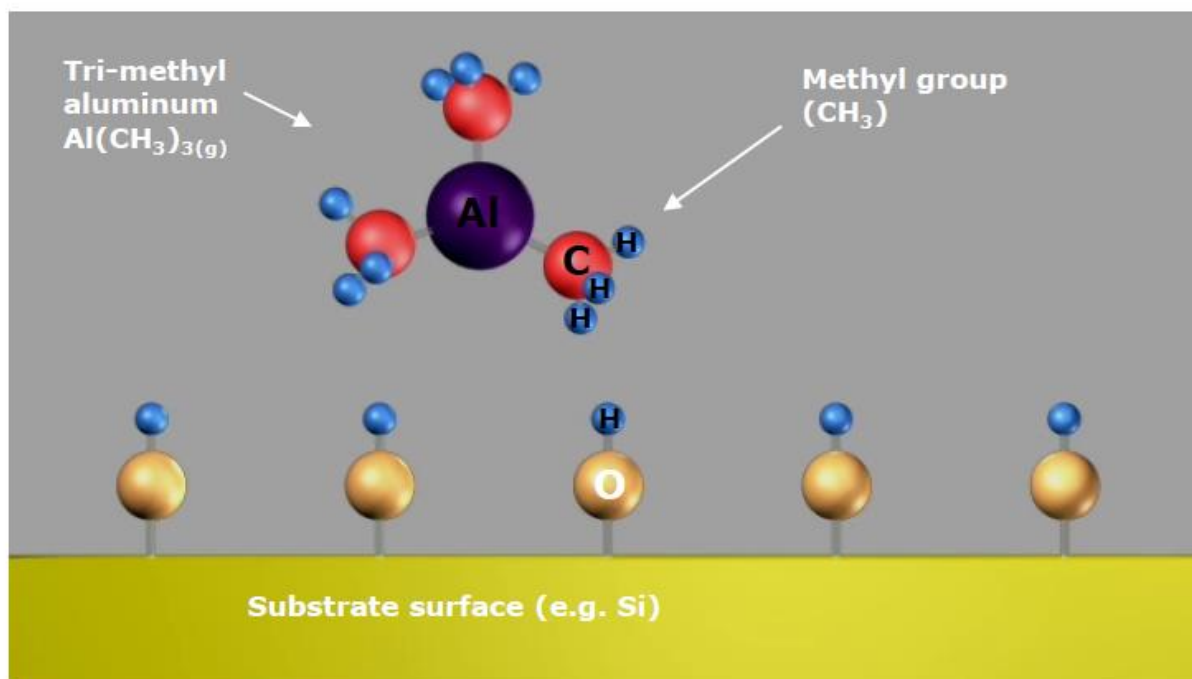
2. Atomic Layer Deposition

30. In an ALD deposition process, at least two reactant vapors are selected that will allow for the controlled, stepwise growth of a thin film on a

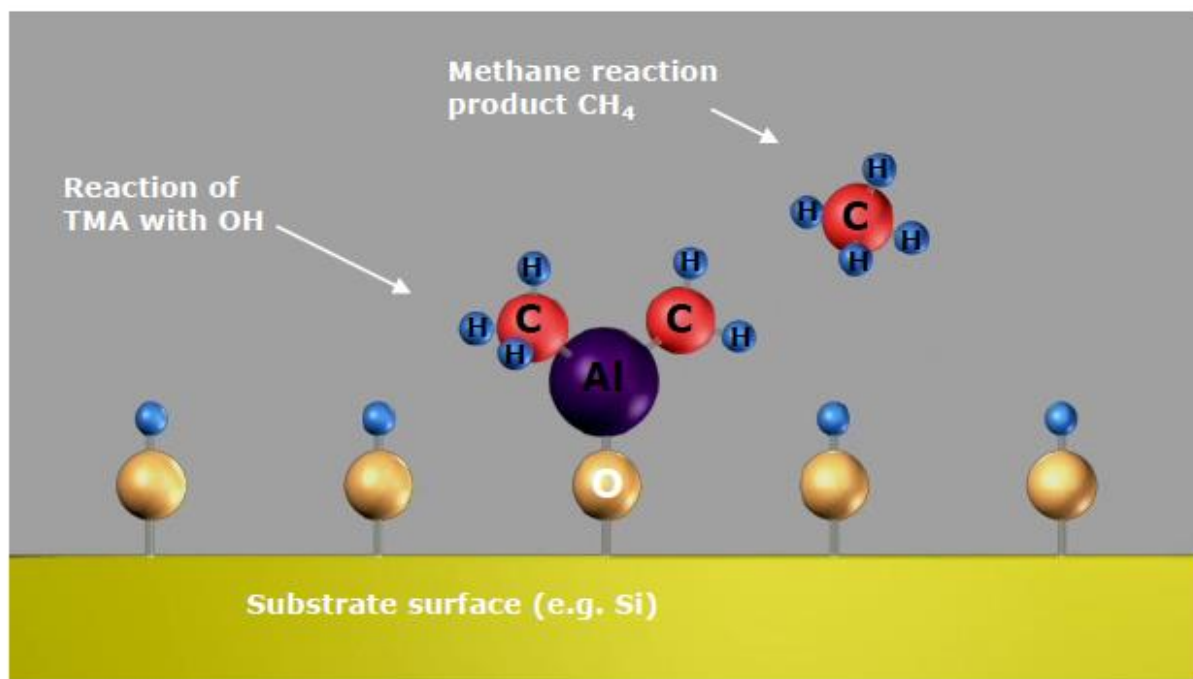
heated surface. *See* Ex. 1013 at 13; Ex. 1001 at 20:56-21:8, 23:54-60, 24:8-15, 24:28-36, 26:44-27:9, 27:45-30:7. In ALD, reactant vapors are alternately exposed to a heated surface in the deposition chamber. *Id.* ALD avoids the continuous growth found in CVD by keeping the reactant vapors separate and by selecting reactant vapors with particular reactive characteristics. *Id.* Fundamental to ALD is the requirement that the reactant vapors react in a self-limiting manner. Ex. 1013 at 13. As opposed to CVD, ALD reactants must not react with their deposits. Ex. 1013 at 13-15. In ALD, when a first reactant vapor is exposed to a heated surface the first reactant vapor will react with available sites on the surface, forming deposits. Ex. 1001 at 20:56-40. Because the first reactant vapor does not react with its deposits, over time, the surface will become saturated and the reactions will stop. Ex. 1001 at 19:34-36; 22:20-26; 27:10-23. Once the deposition chamber is cleared of first reactant vapors and reaction by-products, a second reactant vapor is introduced. Ex. 1001 at 20:56-21:8; Ex. 1013 at 13. The second reactant vapor reacts with the surface sites, now containing the deposited first reactant vapor, and again, over time, the surface will become saturated and the reactions will stop. *Id.* The reactant vapors are selected such that cycles of the alternate exposure of a heated surface to the reactant vapors will result in a film formed by controlled layering of deposits. *Id.*

31. An advantage of ALD is that it can produce films having a uniform thickness over large areas even when the substrate surface exhibits features having complex shapes, such as a trench. Ex. 1001 at 2:35-38, 26:44-27:36, Ex. 1013 at 13; Ex. 1045 at 7. The self-limiting nature of the reactant vapors also allows for a more predictable thickness. *Id.* If the heated substrate surface is allowed to reach saturation during each exposure to the precursor vapors, a characteristic layer thickness will be deposited during each ALD cycle. *Id.* This allows the overall film thickness to be determined accurately from the number of ALD cycles. *Id.*

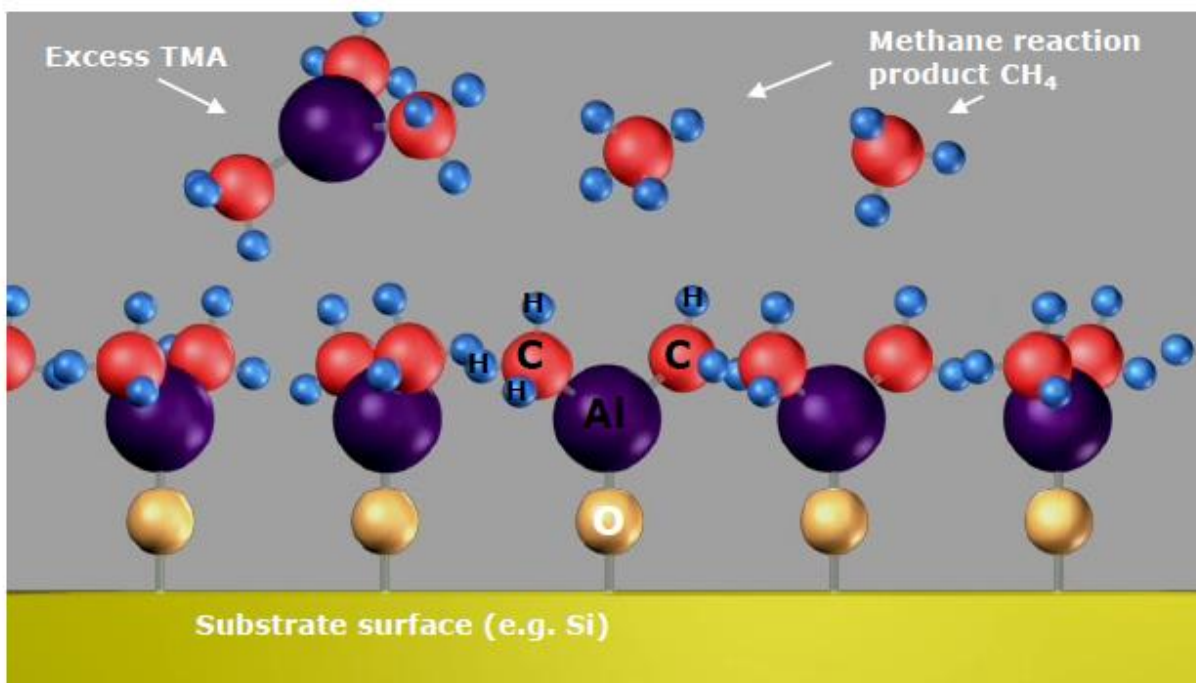
32. I often use demonstrative illustrations while teaching my students basic concepts, and similarly, I have found the following figures from a Stanford University ALD tutorial helpful in explaining the ALD deposition process. The figures in paragraphs 32-37 provide expanded views of the individual steps involved in the ALD of aluminum oxide thin films using trimethylaluminum, $\text{Al}(\text{CH}_3)_3$ – abbreviated TMA, and water, H_2O , as the first and second reactant components, respectively. Ex. 2115, Provine at 4-10. The first figure shows TMA approaching the surface from the gas phase. The surface is coated with hydroxyl (OH) groups originating from water.



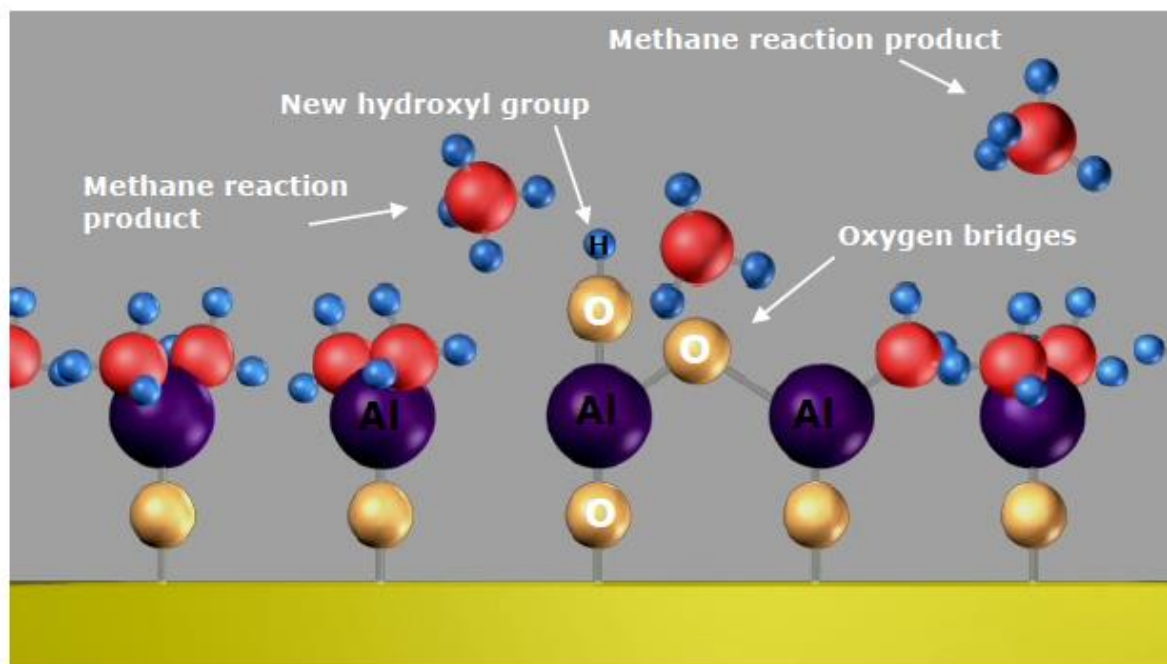
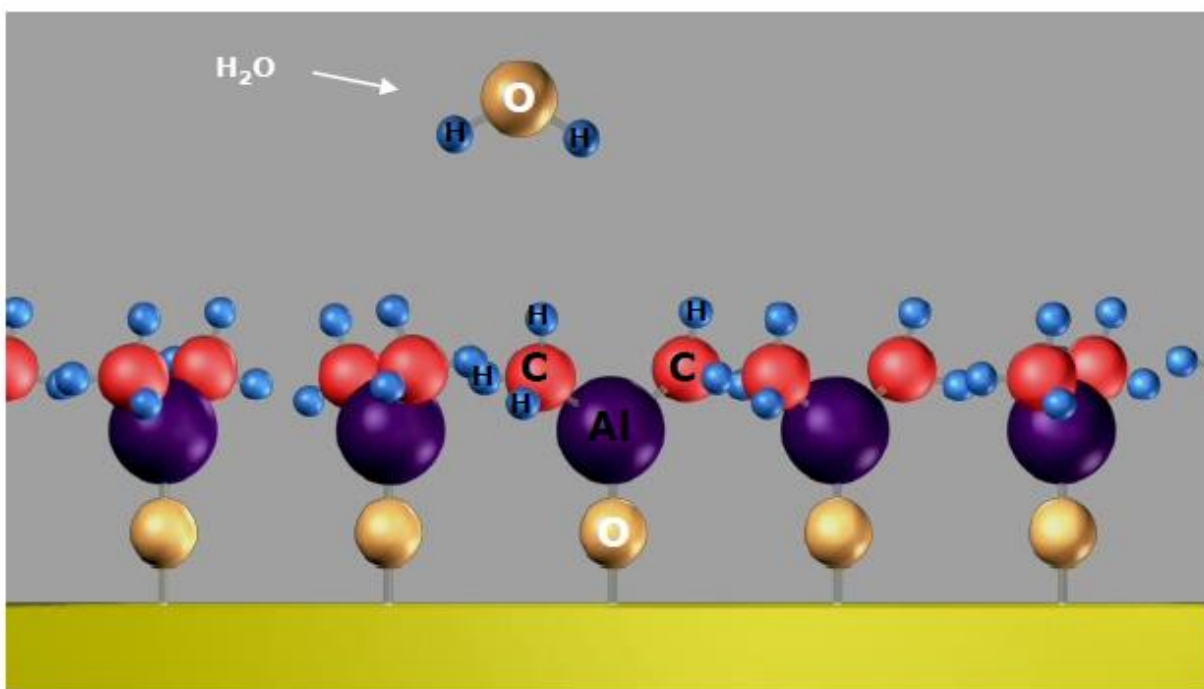
33. Reaction of TMA with a surface hydroxyl results in elimination of gaseous methane (CH₄) and binding of the aluminum fragment to the surface. *Id.* at 5.



34. Similar reactions occur until no hydroxyl groups remain. At this point the surface is saturated with TMA, the first reactant component. Excess TMA will continue to collide with the surface but no further reaction occurs. Along with methane excess TMA is swept out of the reactor. *Id.* at 6.

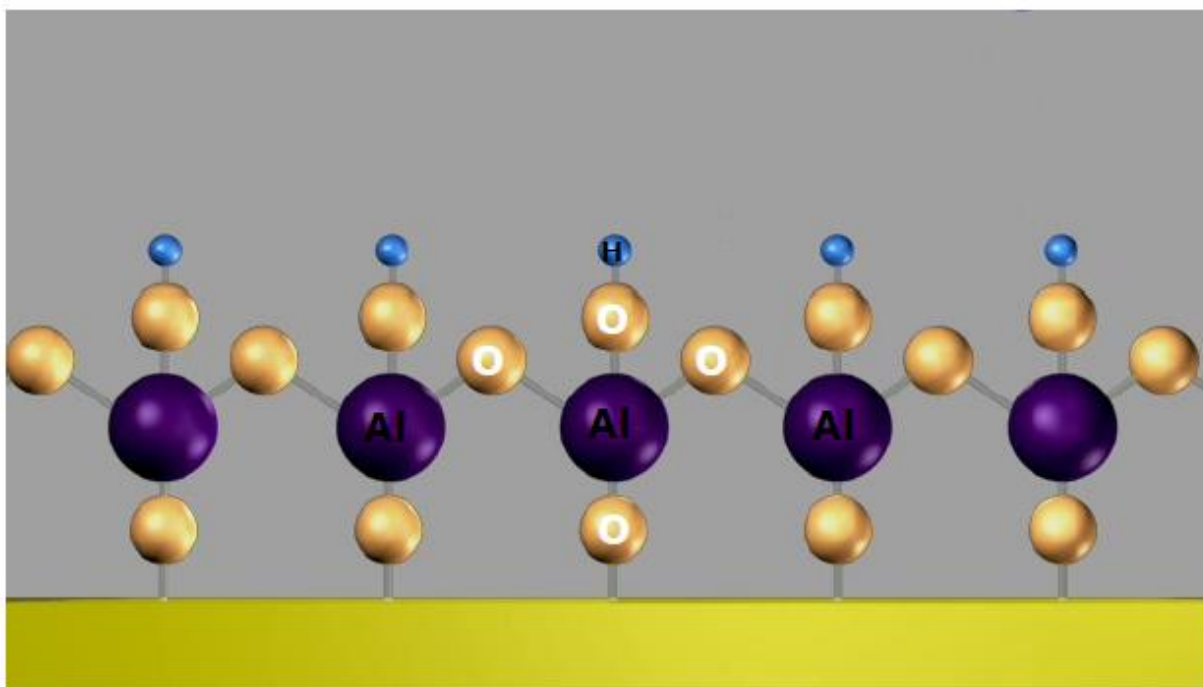


35. After the excess TMA is removed, water vapor, the second reactant component, is introduced into the reactor where it reacts with the methyl (CH_3) groups attached to the aluminum. The reaction produces methane and leaves behind a hydroxyl group bound to the surface. Some of the surface hydroxyl groups will react with adjacent methyl groups to eliminate another methane and form an oxygen bridge between two aluminum atoms. *Id.* at 7.

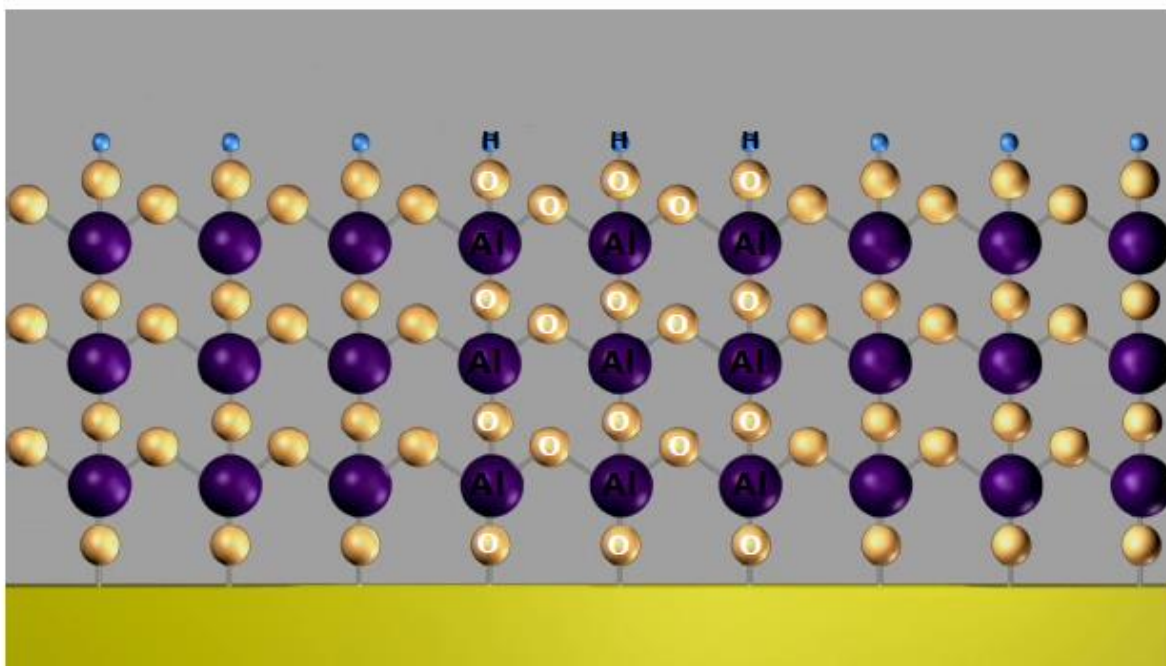


36. After all of the methyl groups have reacted with water, the surface is saturated with hydroxyl groups and excess water is swept from the reactor along

with methane. This completes the first full ALD cycle. However, saturation is not required (and hence not all methyl groups have to react) for an ALD process to take place. The surface shown in the figure below has hydroxyls available for reaction with TMA as the second ALD cycle is started. *Id.* at 9.



37. Repeating the cycle outlined in paragraphs 32-36 results in the formation of a thin film of amorphous aluminum oxide. The film thickness is controlled by the number of ALD cycles. *Id.* at 10.



38. At this point, I am compelled to point out several misleading and inaccurate statements made by Dr. Banerjee in the Banerjee Declarations (Ex. 1003) and by extension in the Petitions.

39. For example, the Petitions misleadingly state that ALD techniques were “well known” at the time of the inventions in the late 1990’s. *See, e.g.*, ’663 Petition at 7. However, it is more accurate to note that although ALD was developed in the seventies in Finland, by the late 90’s there were “a lot of challenges and development work to be done before ALD” could be accepted for microelectronics. Ex. 1013 at 13, 21-22. Specifically, work needed to be done in precursor chemistry development. *Id.*

40. Additionally, the Petitions incorrectly state that “[b]efore 2000, the art had described and/or taught ALD to form metal oxides using metal dialkylamide precursors.” *See, e.g.*, ’663 Petition at 11. This statement is simply not true based on my own experience and as acknowledged by the patent examiner’s reasons for allowance in the continuation application leading to the ’016 Patent. *See* Ex. 1002 at 50. The Petitions cite as alleged support for this false statement certain paragraphs in the Banerjee Declarations that discuss the Buchanan and Vaartstra references as well as the Buchanan reference itself. *See, e.g.*, ’663 Petition at 11. As will be discussed further below, neither Buchanan or Vaartstra disclose the inventions of the ’016 Patent, specifically they do not teach, disclose, or suggest using ALD to form metal oxides using metal dialkylamide precursors.

41. Further, the Petitioner provides a misleading statement regarding what was known by those of skill in the art by the mid-1990s. Specifically, Petitioner asserts that “metal dialkylamides possessed qualities that made them desirable precursors for ALD processes.” *See, e.g.*, ’663 Petition at 12-13 (identifying precursor volatility, thermal stability, and high reactivity as desirable characteristics for ALD). Although these characteristics are desirable, a person of ordinary skill in the art would know that they are not indicative of whether a specific precursor would be suitable for CVD or ALD.

42. As discussed more fully below, in my opinion, a person of ordinary skill in the art did not know that metal dialkylamides were useful for all ALD processes including forming metal oxide films. See Ex. 1013 at 13-22; Ex. 1002 at 50. Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting with any reasonable degree of confidence how a given compound will behave. See Ex. 2102, Jones.

43. Additionally, much of the prior work with dialkylamido metal complexes in CVD teaches away from the use of metal alkylamides in ALD. See Ex. 2103, Fix; Ex. 2104, Ishihara; Ex. 2105, Dubois '92; Ex. 2106, Dubois '94. The prior work using dialkylamido metal complexes in CVD teaches away because it shows that dialkylamido metal complexes react with surfaces to deposit both nitrogen and carbon along with the metal. Both nitrogen and carbon found in the resulting film are considered impurities that should be avoided.

44. A person of ordinary skill in the art charged with devising a new ALD process to deposit a metal oxide film at the time of the invention, including for example HfO_2 , would have been disinclined to consider using a metal alkylamide precursor because he or she would have sought to avoid precursors that would trap both carbon and nitrogen into the film, as unwanted impurities. A person of ordinary skill in the art would have understood that in ALD, the dialkylamido

metal precursor is pulsed into the reactor in the absence of the second reactant (e.g., water). He or she would realize that when the dialkylamido metal precursor is adsorbed onto the surface before the second reactant is added, its carbon and nitrogen atoms could undergo undesirable side reactions leading to carbon and nitrogen incorporation (i.e., impurities in the case of a metal oxide) into the film.

45. Finally, the Banerjee Declaration misleadingly states that a person of ordinary skill in the art at the time of the invention, when tasked with forming metal oxides with ALD, “often looked to precursors that had been successfully used in CVD processes to form metal oxides.” Ex. 1003 at ¶ 72. This implies a false premise that CVD and ALD precursors were interchangeable. While precursors for both CVD and ALD share practical similarities, including the need for volatility, storage stability, and safety, it was widely known that the requirements of ALD precursors are different from CVD precursors. Ex. 1013 at 13; Ex. 2102 at 1. There are many examples of CVD precursors that turn out not to be effective for ALD. *See generally* Ex. 2102. In addition, as noted above there would be concerns about the incorporation of impurities into the film which would cause a person of ordinary skill to avoid using certain precursors.

B. The '016 Patent

46. The title of the '016 Patent is “Vapor Deposition of Metal Oxides, Silicates and Phosphates, and Silicon Dioxide.” Ex. 1001. The inventions claimed

by the '016 Patent include novel processes and materials for deposition of thin films that contain metal oxides, silicates, metal phosphates, or silicon dioxide. Ex. 1001 at 1:22-28.

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

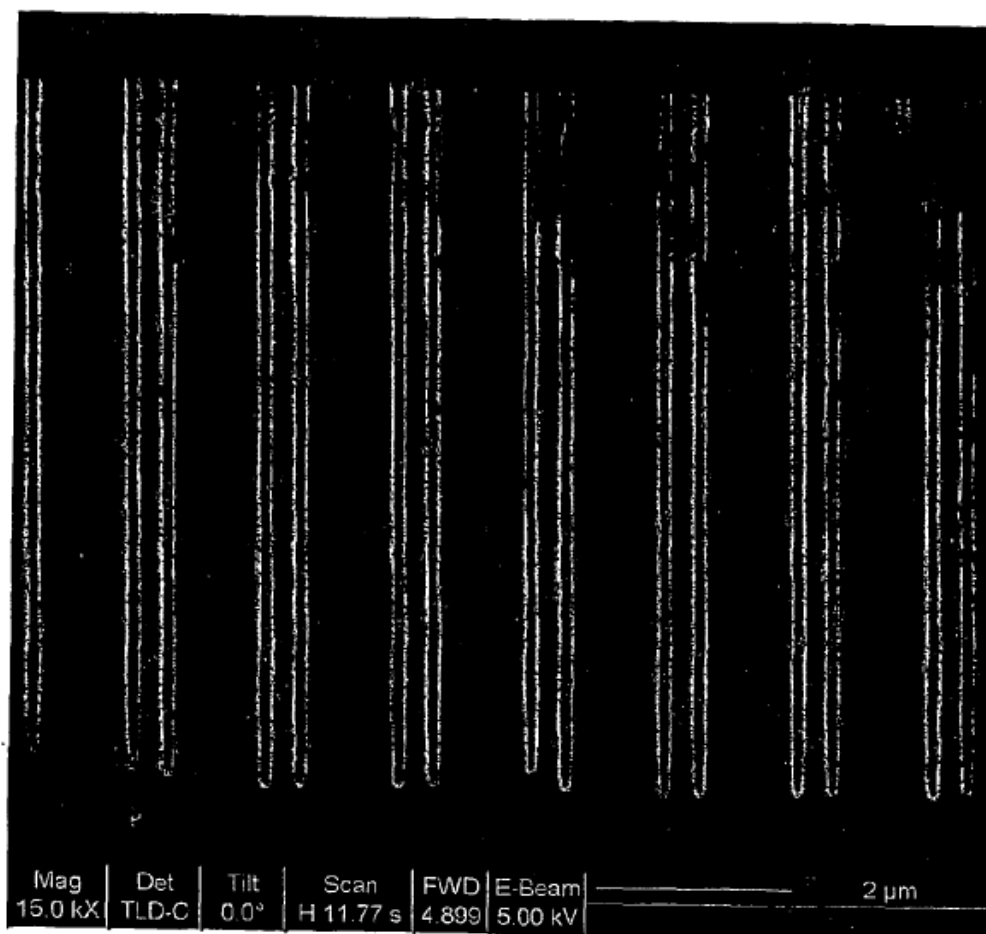
48. Additional problems were encountered when forming dielectric materials in deep trench structures, such as dynamic random access memory (DRAM) devices. See Ex. 1054 at 3; Ex. 1043 at 6-7; Ex. 2107, '848 FH at 2-4; '663 Banerjee Decl. Ex. 1003 at ¶ 69. Not only must the capacitance values remain at a certain level despite the reduction in size, the precursors must be delivered deep into the trenches without a premature reaction that would preclude uniform coverage within the entire deep trench structure. See Ex. 1054 at 3; Ex. 1043 at 6-7; Ex. 2107 at 2-4; '663 Banerjee Decl. Ex. 1003 at ¶ 69.

49. No solution for coating surfaces of deep trenches with high dielectric materials was even expected until 2008. *See* Ex. 2107 at 2-4. ITRS is a set of documents produced by a group of semiconductor industry experts, and is meant to represent the best opinion of these experts on the directions of research up to about 15 years into the future. Ex. 2107 at 2-4; Ex. 1054 at 1. As shown in the ITRS table for DRAM trench Capacitor Films Technology Requirements (Ex. 2108, ITRS), high dielectric material for the year 2008 is highlighted, indicating no satisfactory working solution existed as of 2000 and the roadmap is working towards a solution to occur by year 2008. *See id.* In other words, near the effective filing date of the present application, a group of semiconductor industry experts believed that the high-dielectric material problem would not be solved for at least another eight years.

50. The ALD processes and materials claimed by the '016 Patent solve some of the problems associated with the production of microelectronic devices at smaller sizes. *See* Ex. 1001 at 2:14-52. The inventions claimed by the '016 Patent provide a viable solution for the microelectronic devices industry, including a solution to forming dielectric materials in deep-trench structures, such as those found in DRAM devices. *See* Ex. 1001 at FIG. 3, 2:14-52, 19:41-48, 6:33-35, 27:18-35, 30:9-44.

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

Fig. 3



52. The '016 Patent applicants noted the surprising result of the claimed use of metal alkylamide precursors in ALD to form highly uniform films of metal oxide in holes with very high aspect ratios. See Ex. 1001 at 19:41-48. By contrast,

the prior art ALD precursors were not able to deposit uniform films in such high aspect ratios. *Id.*

V. OPINION ON CLAIM CONSTRUCTION

53. I understand that claim construction is the common terminology used to describe the interpretation of claim terms. It is also my understanding that in this *inter partes* review proceeding, the claim terms are to be given their broadest reasonable interpretation consistent with the specification and file history of the '539 Patent, as understood by one of ordinary skill in the art.

VI. OPINIONS ON IPR2017-00663

A. Grounds Based on Buchanan² and Min

54. It is my understanding that the Petitioner has alleged that Buchanan in view of Min renders obvious Claims 1-3, 5-7, and 9-10 of the '016 Patent. '663 Petition at 4. Having reviewed, among other things, Buchanan, Min, the '663 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Buchanan in view of Min, as presented by the Petitioner, does not render obvious Claims 1-3, 5-7, and 9-10 of the '016 Patent.

1. Summary of the Asserted References

² I note that Buchanan references one of my papers in its specification. Ex. 1005 at 2:56-58 (referencing D. G. Colombo, D. C. Gilmer, V. G. Young, S. A. Campbell and W. L. Gladfelter Chem. Vap. Dep. 1998, 4, No. 6, 1998 P. 220.).

a. U.S. Patent No. 6,984,591, “Precursor Source Mixtures” (Buchanan)

55. Buchanan discloses the use of an inert organic liquid as a solvent in which a precursor compound can be dissolved, emulsified, or suspended to form a precursor mixture for use in a CVD or an ALD deposition method. Ex. 1005 at Abstract, 3:56-4:21, 29:14-34:30 (Claims 1-45, all requiring an inert “organic” liquid). Buchanan indicates that “[m]ost films deposited by CVD or ALD for semiconductor applications are grown using conventional bubbler technology with a carrier gas bubbled through a neat (i.e., without solvent) precursor at an elevated temperature, relying on the vapor pressure of the precursor to be constant in order to deliver a uniform precursor flux to the film.” *Id.* at 1:28-33. Buchanan points out that the conventional bubbler technology suffers from a number of shortcomings. For example, Buchanan explains that “because vapor pressure is directly related to temperature, conventional bubbler technology suffers from the disadvantage of needing to maintain a bubbler temperature with minimal variation during a run or from run to run.” *Id.* at 1:33-37. Buchanan indicates that “[f]luctuations in precursor flux are known to result in variable film growth rates.” *Id.* at 1:37-39. Further, Buchanan indicates that “[e]levated temperatures and thermal cycling of a precursor during vaporization in a conventional bubbler may contribute to premature degradation of the precursor over time.” *Id.* at 1:46-48.

56. Buchanan's contribution for solving the above problems of conventional systems for the delivery of precursors to an ALD or a CVD reactor involves dissolving, emulsifying or suspending one or more precursors in an inert organic liquid to form a precursor source mixture. *See, e.g., id.* at 29:13-35 (Claim 1). The precursor in the precursor source mixture can be vaporized and a constituent of the vaporized precursor can be deposited on a substrate to form a film. *Id.* at 4:24-28. Buchanan indicates that "the inert liquid, may or may not be co-vaporized with the precursor." *Id.* at 4:28-29. In connection with its central teaching regarding the formation of a precursor mixture to enhance the delivery of a precursor to an ALD or a CVD reactor, Buchanan provides a list of tens of thousands of precursors that can be used to form a precursor mixture, presumably to indicate that its teachings regarding the use of an inert liquid is applicable to a variety of different precursors.

57. More specifically, Buchanan's precursor source mixture is comprised of at least one precursor composed of a metal, which is bound to at least one ligand, dissolved, emulsified or suspended in an inert organic liquid. *Id.* at Abstract, 3:56-4:21, 29:14-34:30 (Claims 1-45, all requiring an inert "organic" liquid).

58. Buchanan discloses a large number of elements, ligands, and inert organic liquids that can be combined to form a precursor source mixture. For example, Buchanan discloses that its source mixture can include:

at least one precursor composed of an element selected from the group consisting of Li, Na, K, Rb, Cs, Fr, Be, Mg, Ti, Zr, Hf, Sc, Y, La, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, P, Sb and Bi, to which is bound at least one ligand selected from the group consisting of hydride, alkyl, alkenyl, cycloalkenyl, aryl, alkyne, carbonyl, amido, imido, hydrazido, phosphido, nitrosyl, nitril, nitrate, nitrile, halide, azide, alkoxy, siloxy, silyl, and halogenated, sulfonated or silylated derivatives thereof, which is dissolved, emulsified or suspended in an inert liquid selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkyl nitrile, halogenated hydrocarbons, silylated hydrocarbons, thioethers, amines, cyanates, isocyanates, thiocyanates, silicone oils, nitroalkyl, alkyl nitrate, and mixtures thereof. The precursor source mixture may be a solution, emulsion or suspension and may consist of a mixture of solid, liquid and gas phases which are distributed throughout the mixture.”

Id. at Abstract.

59. Buchanan goes on to provide “specific details of the present invention.” *See id.* at 8:45-47. In the “specific details” section, Buchanan identifies ten (10) classes of precursor source mixtures. *See id.* at 8:45-18:34 (“Precursor Source Mixtures for Hydride-Containing Compounds,” “Precursor

Source Mixtures for Alkyl-Containing Compounds,” “Precursor Source Mixtures for Alkenyl-Containing Compounds,” “Precursor Source Mixtures for Carbonyl-Containing Compounds,” “Precursor Source Mixtures for Alkoxy-Containing Compound,” “Precursor Source Mixtures for Amino-Containing Compound,” “Precursor Source Mixtures for Phosphido-Containing Compound,” “Precursor Source Mixtures for Nitrate-Containing Compound,” “Precursor Source Mixtures for Halide-Containing Compounds,” and “Precursor Source Mixtures for Silyl-Containing Compounds”).

60. In each of the ten (10) classes of precursor source mixtures, Buchanan discloses “preferred precursors” for use in its precursor source mixture. *See id.* For example, the first class of precursor source mixtures identified is “Precursor Source Mixtures for Hydride-Containing Compounds.” *See id.* at 8:50-9:55. As identified by Buchanan:

Preferred precursor source mixtures of hydride-containing compounds are comprised of:

(i.) $MR_1 x R_2 y Az$

where M is an element selected from the group consisting of Li, Na, K, Rb, Cs, Fr, Be, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb and Bi, preferably B, Al, Ga, In, As, Sb, Si, Ge, Sn, Pb, Zn, Cd and Hg; R₁ is a hydride; R₂ is a ligand selected from the group consisting of hydride, alkyl, alkenyl, cycloalkenyl, aryl, alkyne, carbonyl, amido, imido,

hydrazido, phosphido, nitrosyl, nitryl, nitrate, nitrile, halide, azide, alkoxy, siloxy, silyl, and/or halogenated, sulfonated or silyated derivatives thereof, R1 and R2 may or may not be identical ligands; A is an optional coordinatively bound ligand selected from the group consisting of phosphines, phosphites, aryls, amines, arsines, stibenes, ethers, sulfides, nitrites, isonitriles, alkenes, alkynes, hydrazine, pyridines, nitrogen heterocycles, macrocycles, schiff bases, cycloalkenes, alcohols, phosphine oxides, alkylidenes, nitrites, and water; $x \geq 1$; $y \geq 0$; z is ≥ 0 ; and $x+y$ =the valence of element M.

(ii.) inert liquid

wherein the inert liquid is selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkyl nitrile, halogenated hydrocarbons, silyated hydrocarbons, thioethers, amines, cyanates, isocyanates, thiocyanates, silicone oils, nitroalkyl, alkyl nitrate and/or mixtures of one or more of the above. Preferably, the inert liquid is composed essentially of a C5–C12 alkane.

(iii.) optional additive

Id. The description above is representative of the description provided for each of the nine (9) remaining classes of precursor source mixtures. *See id.* at 8:45-18:34.

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

61. Min is directed to the investigation of atomic layer deposition (ALD) of amorphous TiN films on SiO₂ using the reactant sources

tetrakis(ethylmethylamino)titanium ($\text{Ti}[\text{N}(\text{C}_2\text{H}_5\text{CH}_3)]_4$ aka “TEMAT”) and ammonia (NH_3). Ex. 1006 at Abstract. Min found that TiN films could be formed on SiO_2 using ALD with the reactants TEMAT and NH_3 , as long as the ALD process was maintained within a specific temperature range. *Id.* at Abstract, 8. Specifically, Min found that TiN ALD required a definite temperature range between 170°C and 210°C . *Id.* at 8. The definite temperature range is required to prevent TEMAT from decomposing thermally so that a monolayer can be chemisorbed on the surfaces. *See id.*

62. To investigate the formation of a TiN film using TiN ALD, Min also investigated CVD using just TEMAT and also CVD using TEMAT and NH_3 . *Id.* at 8, FIG. 3. By evaluating the results, Min was able to establish that TiN ALD exhibited the appropriate film growth between 170°C and 210°C . *See id.* at 8. Min found that at around 230°C TiN ALD transitioned to CVD. *See id.* (“By combining results from (a) and (b), it is shown that the transition temperature from ALD to MOCVD is around 230°C . Therefore, the temperature range for TiN ALD is limited to below 230°C .”)

63. Min also found that ALD using TEMAT and NH_3 resulted in different deposition of the TiN films. *See id.* (“Although TiN films were deposited using TEMAT and NH_3 in both (a) and (c), different deposition results are observed.”). Min found that the different deposition results were caused by gas phase reactions

in the CVD process. *Id.* The addition of NH_3 to TEMAT in CVD led to gas phase facile transamination reactions. *Id.*

64. In comparing the TiN ALD process with the two TiN CVD processes, Min also found that NH_3 has a profound effect on the carbon contamination levels found in the resulting film. *Id.* at 10. Min found that single source precursor CVD using TEMAT (i.e., CVD using only TEMAT as a reactant) led to films with 25 at.% (atomic percent) of carbon contamination. *Id.* Contamination was reduced to 5 at.%, and below 4 at.% when using CVD with both TEMAT and NH_3 , and using ALD with TEMAT and NH_3 , respectively. *See id.*

2. Petitioner's Proposed Combination of Buchanan and Min Does Not Teach or Render Obvious Claims 1-3, 5-7, and 10

65. In my opinion, Petitioner's proposed combination of Buchanan and Min does not teach or render obvious Claims 1-3, 5-7, 9-10 of the '016 Patent.

66. Claim 1 of the '016 Patent recites a self-limiting ALD process using a metal alkylamide precursor as the first reactant to form a metal oxide film. *See Ex. 1001 at 30:9-26 (Claim 1); see also '663 Petition at 13 (identifying that Claim 1 of the '016 Patent is a self-limiting ALD process), 37-39 (interpreting Claim 1 to use a metal alkylamide precursor as the first reactant in its ALD process), 41 (interpreting the ALD process of Claim 1 to form a metal oxide film).* I understand that Claims 2-3, 5-7, 9-10 of the '016 Patent are dependent claims, and therefore,

include all of the elements of the claims from which they depend, as well as their own recited claim elements.

67. I understand that Petitioner alleges that Buchanan discloses “most or all of the elements of Claims 1-3, 5-7, 9-10 of the 016 Patent.” ’663 Petition at 30. I further understand that Petitioner alleges that to the extent that Buchanan does not disclose all of the elements of Claim 1, the only element not disclosed in Buchanan is a self-limiting ALD process. *Id.* at 31. Petitioner alleges that to the extent a self-limiting ALD process using a metal alkylamide to form a metal oxide film is not disclosed in Buchanan, it would have been obvious in view of Min. *Id.* I disagree with Petitioner’s allegations.

68. In my opinion, a person of ordinary skill in the art would not have found Buchanan alone or in combination with Min to disclose or render obvious Claim 1 of the 016 Patent. First, a person of ordinary skill in the art would not have understood Buchanan to disclose or render obvious a self-limiting ALD process using a metal alkylamide precursor to produce a metal oxide film. Second, a person of ordinary skill in the art would have had no motivation to combine the teachings of Buchanan and Min to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film

69. Further, as I discuss below, a person of ordinary skill in the art would not have looked to combined Buchanan with Min to arrive at a process that meets all of the recited elements of Claims 2-3, 5-7, 9-10 of the '016 Patent.

a. The Combination of Buchanan and Min Fails to Disclose or Render Obvious a Self-Limiting ALD Process Using a Metal Alkylamide Precursor to Form a Metal Oxide Film.

70. The Petitioner argues that Buchanan alone or in combination with Min discloses or renders obvious a self-limiting ALD process using a metal alkylamide precursor to form a metal oxide film. *See* '663 Petition at 36-49. First, Petitioner argues that Buchanan alone discloses such a process. *Id.* at 36-38. Second, Petitioner argues that if no such disclosure exists in Buchanan, it would have been obvious to modify Buchanan's Example 3, in view of Min, to arrive at such a process. *Id.* Third, the Petitioner argues that a person of ordinary skill in the art, having knowledge of Min, would have been motivated to modify Min's ALD process based on Buchanan's teachings to arrive at such a process. *Id.* at 38. I disagree. For the reasons discussed below, it is my opinion that the combination of Buchanan and Min fails to disclose or render obvious a self-limiting ALD process using a metal alkylamide precursor to form a metal oxide film.

71. First, in my opinion, Petitioner's conclusions are based on a mischaracterization of Buchanan's teachings regarding its disclosed metal

dialkylamide precursors. For each of Petitioner's three arguments identified above, the Petitioner appears to rely on Buchanan's use of the designation "highly preferred" to suggest that the metal dialkylamide precursors identified in Buchanan are "highly preferred" precursors for use in ALD to form metal oxides. See '663 Petition at 36-39. However, Buchanan provides no such teaching or suggestion. Rather, as discussed in more detail below, Buchanan discloses tens of thousands of precursors for use in a CVD or an ALD process to form a number of different films without providing any teaching or suggestion regarding the selection of dialkylamide precursors for use in a self-limiting ALD process to form a metal oxide film. The general description in Buchanan that its precursors can be used in a CVD or an ALD process is not sufficient to conclude that any of its precursors can be used in both a CVD process and an ALD process to form any desired film. In fact, as discussed more fully below, Buchanan discloses certain precursors that would not be suitable for use in an ALD process.

72. Second, Petitioner's arguments are primarily based on Buchanan's Example 3. See '663 Petition at 36-38; 48-53. However, Buchanan's Example 3 makes no mention of metal dialkylamide precursors. See Ex. 1005 at 19:60-20:24. Rather, in Example 3, Buchanan discloses the use of zirconium nitrate and hafnium tertbutoxide. *Id.* Additionally, Buchanan provides no teaching or disclosure that Example 3 can be modified to arrive at self-limiting ALD process to produce a

metal oxide film. *See id.* Further, no such teaching exists in Min. A person of ordinary skill in the art would not have been motivated to modify Example 3 based on Buchanan alone or in view of Min to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film.

73. Third, Petitioner argues that metal dialkylamides had properties that made them advantageous as ALD precursors to produce a metal oxide film. *See* '663 Petition at 38; 50. In particular, Petitioner identifies that metal dialkylamides are volatile, thermally stable, and highly reactive. *Id.* at 50. In my opinion, Petitioner's argument ignores the state of the art at the time of Buchanan, Min and the '016 Patent. A person of ordinary skill in the art would have understood that it is not possible to ascertain whether a precursor can be successfully used in an ALD process to produce a metal oxide film without extensive experimentation. A person of ordinary skill in the art would have understood that volatility, thermal stability, and high reactivity are useful characteristics for precursors in both CVD and ALD. However, the fact that a precursor exhibited these characteristics would not provide a reasonable expectation that the precursor could have been successfully employed in a CVD or an ALD process to produce a metal oxide film.

74. Fourth, the state of the art at the time of Buchanan, Min and the '016 Patent would have dissuaded one of ordinary skill in the art from using metal dialkylamides in an ALD process to form a metal oxide film. This is so because it

was known that the use of metal dialkylamide precursors in a CVD process for forming a metal oxide film could lead to significant carbon and nitrogen contamination of the film. A person of ordinary skill in the art would have considered that the alternate introduction of one or more metal dialkylamide precursor(s) into an ALD reactor would result in the adsorption of the precursor on the growing film with the potential for both carbon and nitrogen atoms of the precursor to be incorporated into the film, as unwanted impurities. Additionally, a person of ordinary skill would have appreciated that Buchanan's reliance on inert organic solutions for its precursors would have added complexity to the deposition reaction and could have led to even further carbon contamination. See Ex. 1005 at Abstract, 4:1-21 (requiring the use of inert organic solutions).

(1) Buchanan does not disclose or render obvious a self-limiting ALD process using a metal dialkylamide to form a metal oxide film

75. A person of ordinary skill in the art would not understand Buchanan to disclose or render obvious the use of a metal dialkylamide in a self-limiting ALD process to form a metal oxide film. Buchanan is directed to precursor source mixtures formed by any combination of a myriad of metals, ligands, and solutions. Ex. 1005 at Abstract. Buchanan states:

A precursor source mixture useful for CVD or ALD of a film comprising: at least one precursor composed of an element selected from the group consisting of Li, Na, K,

Rb, Cs, Fr, Be, Mg, Ti, Zr, Hf, Sc, Y, La, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, P, Sb and Bi, to which is bound at least one ligand selected from the group consisting of hydride, alkyl, alkenyl, cycloalkenyl, aryl, alkyne, carbonyl, amido, imido, hydrazido, phosphido, nitrosyl, nitryl, nitrate, nitrile, halide, azide, alkoxy, siloxy, silyl, and halogenated, sulfonated or silylated derivatives thereof, which is dissolved, emulsified or suspended in an inert liquid selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkylnitrile, halogenated hydrocarbons, silylated hydrocarbons, thioethers, amines, cyanates, isocyanates, thiocyanates, silicone oils, nitroalkyl, alkylnitrate, and mixtures thereof. The precursor source mixture may be a solution, emulsion or suspension and may consist of a mixture of solid, liquid and gas phases which are distributed throughout the mixture.

Id. Buchanan further discloses that a film can be formed on a substrate using a precursor source mixture in a CVD or an ALD process. Ex. 1005 at Abstract, 7:41-43. For example, Buchanan discloses the formation of metal, metal oxide, metal nitride, and metal silicide containing films. *See, e.g.*, Ex. 1005 at 18:40-29:10 (Examples 1-17).

76. Buchanan's disclosure of such an extraordinary number of potential precursor mixtures combined with the added possibilities of using CVD or ALD to create one of four types of films would not have taught or directed a person of ordinary skill to any particular precursor for use in an ALD process to deposit a

metal oxide film, let alone a metal dialkylamide precursor for use in an ALD process to form a metal oxide, as required by Claim 1.

77. Petitioner relies extensively on Buchanan's designation of "highly preferred" precursors to allege that Buchanan discloses or renders obvious an ALD process to deposit a metal oxide film using a dialkylamide precursor. See '663 Petition at 37-39;48-52 (continually referring to Buchanan's "highly preferred" designation.") However, in my opinion, Petitioner's reliance on the term "highly preferred" is misplaced. Buchanan's use of the term "highly preferred" with regard to certain precursors would not render such a specific process obvious due to the sheer number of precursor options proposed and because Buchanan does not provide any guidance regarding the suitability of the "highly preferred" for a specific deposition technique or for the creation of a specific type of film.

(a) Buchanan's "highly preferred" designation would not direct a person of ordinary skill in the art to metal dialkylamides

78. In my opinion, a person of ordinary skill in the art would not have understood Buchanan's "highly preferred" designation to provide any guidance toward the use of a metal dialkylamide precursor in an ALD process to deposit a metal oxide film because of the sheer number of precursor options disclosed in Buchanan.

[illegible]

80. Buchanan’s disclosure of “preferred precursors” expands even further when each precursor is considered individually. Buchanan’s list of “preferred precursors” is a mix-and-match of ligands and metals. *Id.* For example, one set of “preferred precursors” includes “trimethyl-, triethyl-, triisobutyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or ethyldimethyl-B, Al, Ga, In, As or Sb.” *Id.* at 6:4-6:6. Buchanan appears to identify that any one of the eight (8) ligand groups (trimethyl-, triethyl-, triisobutyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or ethyldimethyl,) can be combined with any one of the six (6) elements (B, Al, Ga, In, As, or Sb), leading to forty-eight (48) separate “preferred precursors” from this one set. *Id.* In the same paragraph, Buchanan expands this list of “highly preferred precursors” by combining the “dimethyl-, diethyl-, diisobutyl-B, Al, Ga, In, As or Sb” fragments with “hydride, chloride, fluoride, bromide, iodide, Cp, amide, dimethylamide or azide”, thus adding another 162 compounds. *Id.* at 6:7-11.

81. Petitioner appears to ignore this full list of “preferred precursors,” and narrowly focuses on Buchanan’s disclosure of “highly preferred” amino-containing precursors, which include two dialkylamide compounds. See ’663 Petition at 37-38. In my opinion, a person of ordinary skill would have no reason to focus on these “highly preferred” precursors based on the disclosures in Buchanan.

82. In my opinion, one of ordinary skill in the art would have had no reason to narrowly focus on “highly preferred” amino-containing precursors for their use in an ALD process, much less in an ALD process for forming an oxide film. Buchanan’s class of amino-containing precursors is only one of ten (1/10) separate classes of precursors disclosed in Buchanan. See Ex. 1005 at 8:50-18:34 (“Precursor Source Mixtures for Hydride-Containing Compounds,” “Precursor Source Mixtures for Alkyl-Containing Compounds,” “Precursor Source Mixtures for Alkenyl-Containing Compounds,” “Precursor Source Mixtures for Carbonyl-Containing Compounds,” “Precursor Source Mixtures for Alkoxy-Containing Compound,” “Precursor Source Mixtures for Amino-Containing Compound,” “Precursor Source Mixtures for Phosphido-Containing Compound,” “Precursor Source Mixtures for Nitrate-Containing Compound,” “Precursor Source Mixtures for Halide-Containing Compounds,” and “Precursor Source Mixtures for Silyl-Containing Compounds”). Additionally, Buchanan provides no explanation regarding why, within those classes, it identifies some precursors as “highly preferred,” as opposed to “preferred.” As such, nothing in Buchanan would direct a person of ordinary skill in the art to focus specifically on amino-containing compounds or to the “highly preferred” designation, especially in connection with forming an oxide film via an ALD process.

83. A person of ordinary skill in the art presented with Buchanan's extensive list of precursors would have no direction to specifically use a metal dialkylamide precursor and additionally, would have no direction to use a metal dialkylamide precursor for use in an ALD process to form a metal oxide, as required by Claim 1.

(b) Buchanan provides no guidance regarding the suitability of its "preferred precursors" for use in a self-limiting ALD process to form a metal oxide film

84. In my opinion, Buchanan's "highly preferred" designation would not have led a person of ordinary skill to modify any disclosure of Buchanan to develop an ALD process to deposit a metal oxide film using a metal dialkylamide precursor. Buchanan offers no guidance to a person of ordinary skill on the suitability of its precursors, including "highly preferred" precursors, for a specific deposition technique or for the creation of a specific film. Buchanan's only description relating to the "highly preferred" precursors is the identification that they are "readily vaporized." See Ex. 1005 at 5:66-67. The mere fact that a precursor can be readily vaporized provides no reasonable expectation that it can be successfully used in an ALD process. In fact, as discussed below, there are examples of vaporizable precursors that cannot be employed in an ALD process.

85. Petitioner attempts to attribute certain characteristics to the “preferred precursors” to argue that a person of ordinary skill would have understood Buchanan to disclose or motivate one: 1) to look to metal dialkylamide precursors, 2) to use those precursors in an ALD process and 3) to use those precursors to create metal oxide films. *See* ’663 Petition at 48-53. I disagree with each of these conclusions and address each one in turn, below.

86. First, a person of ordinary skill would not have been directed by Buchanan to look to metal dialkylamides. Petitioner only focuses on Buchanan’s disclosure of “preferred precursors” for an amino-containing compound. *See* ’663 Petition at 32, 34. Petitioner relies on this narrow focus to argue that Buchanan directs a person of ordinary skill to metal dialkylamides. ’663 Petition at 34. As discussed above, Buchanan identifies ten (10) separate categories of compounds. Ex. 1005 at 8:50-18:34. Buchanan provides no indication that amino-containing compounds are in any way preferable to the other categories. A person of ordinary skill in the art would have no direction from Buchanan to single out metal dialkylamides from the myriad of precursors disclosed in Buchanan.

87. Second, a person of ordinary skill would not have interpreted Buchanan as teaching that metal dialkylamides could be used in an ALD process, let alone to be used in an ALD process to form a metal oxide. Petitioner states that “Buchanan itself states that transition metal dialkylamides (which are ‘one or more

metal amides having an amido group consisting of dialkylamido, disilylamido and (alkyl)(silyl)amido moieties’) are ‘highly preferred’ precursors for ALD.” ‘663 Petition at 34. This statement is simply untrue. Buchanan never specifies that these “preferred precursors” are particularly suited for ALD.

88. In fact, certain of Buchanan’s precursors are not suitable for ALD. As discussed further below, Buchanan’s “preferred precursor” bis(benzene)cobalt (Ex. 1005 at 6:17) is unsuitable for BOTH CVD and ALD processes due to its thermal instability. Additionally, Buchanan discloses tetramethyl-, tetraethyl-, tetraphenyl-, or tetra-n-butyl-Si as “preferred precursors” (Ex. 1005 at 6:7-8). Although volatile, these are remarkably stable compounds. The thermal stability and lack of reactivity of tetramethylsilane render it useless as an ALD precursor. Attempts to use tetramethylsilane in ALD have failed. See Ex. 2112, Hämäläinen.

89. Petitioner argues that Buchanan teaches that any of his precursors, can be used in any CVD or ALD process. ’663 Petition at 49. In essence, Petitioner is alleging that Buchanan teaches that tens of thousands of precursor mixtures are suitable for use in both CVD and ALD processes. See Ex. 1005 at Abstract. I wholly disagree with Petitioner’s interpretation of Buchanan’s teachings. As I identified above, and will discuss more fully in Section VI.A.2.a(2) below, not all of Buchanan’s disclosed precursors are suitable for use in an ALD process.

90. Buchanan indicates that its precursor mixtures are composed of one of fifty (50) elements and at least one ligand selected from twenty (20) ligand groups, in one, or a mixture of inert liquids selected from twenty-one (21) groups of inert liquids. *See* Ex. 1005 at Abstract. Buchanan's identification of so many elements, groups of ligands, and inert liquids with the additional mixture options leads to tens of thousands of precursor mixtures. A person of ordinary skill in the art would have understood that Buchanan's disclosure was meant to illustrate the variety of elements, ligands, and inert liquids that could be used to make Buchanan's claimed precursor mixture. A person of ordinary skill in the art would have known that despite Buchanan's broad disclosure, not every disclosed precursor would be suitable for CVD and ALD. Based on Buchanan's disclosure, a person of ordinary skill in the art would not have known which precursors would lead to successful ALD processes without extensive experimentation of the tens of thousands of identified precursors.

91. Third, a person of ordinary skill in the art would not have interpreted Buchanan to disclose that every precursor mixture could be used to form a suitable metal oxide film. As Petitioner notes, Buchanan identifies that its precursor mixtures can be used to form metal, metal oxide, metal nitride, or metal silicide films. *See* Petition at 25. A person of ordinary skill in the art would have

understood that not all of the tens of thousands of precursor mixtures would be viable to form each of the four identified films.

(c) Buchanan's Example 3 does not render obvious a self-limiting ALD process using a metal alkylamide to form a metal oxide film

92. Petitioner argues that a person of ordinary skill in the art would have been motivated to modify Buchanan's Example 3 to use Buchanan's metal dialkylamide precursors because Example 3 is not limited to the specific precursors used in the example. '663 Petition at 49. Petitioner argues that Buchanan precursors can be used in "any CVD or ALD process" and that a person of ordinary skill in the art would have been motivated to use Buchanan's disclosed metal dialkylamide precursors because "Buchanan expressly teaches that these precursors are preferable." *Id.* at 50. In my opinion, Petitioner's interpretation of Buchanan is incorrect.

93. Buchanan never teaches that its metal dialkylamide precursors are preferable for use in an ALD process to produce a metal oxide film, as alleged by Petitioner. As explained above Buchanan only identifies certain precursors as "preferred precursors" because they are readily vaporized. Ex. 1005 at 5:66-67. Buchanan provides no additional distinction between its "preferred precursors" and its "highly preferred precursors," and does not identify any precursors as preferable for use in a self-limiting ALD process to produce a metal oxide film. Further, as

discussed below in Section VI.A.2.a(2), as person of ordinary skill in the art would understand that not all of Buchanan's disclosed precursors are suitable for CVD and ALD. In fact, at least one precursor disclosed in Buchanan (e.g., bis(benzene)cobalt) is not suitable for use in a CVD or an ALD process.

94. In my opinion, a person of ordinary skill in the art would not have found it obvious to modify Buchanan's Example 3, to arrive at a self-limiting ALD process using a metal alkylamide precursor to form a metal oxide film. First, in my opinion, nothing in Buchanan would direct a person of ordinary skill in the art to modify Example 3 to use a metal alkylamide precursor to form a metal oxide film. Second, nothing in Buchanan would teach or suggest to a person of ordinary skill in the art that such a process could be run using ALD in a self-limiting manner.

95. Petitioner also argues that the person of ordinary skill in the art would have been motivated to use metal dialkylamide precursors in Buchanan's Example 3 "because dialkylamides were known to have characteristics that made them desirable for ALD." '663 Petition at 50. Specifically, Petitioner states, "[o]ne of ordinary skill in the art knew that the metal dialkylamides have characteristics such as stability, volatility, and reactivity and that those characteristics are desirable in ALD processes." *Id.* However, a person of ordinary skill in the art would have known that many compounds share these characteristics. For example, as

discussed above, Buchanan's entire list of "preferred precursors," including all ten (10) categories of "preferred precursors," were identified because they are readily vaporized, (i.e., volatile). Ex. 1005 at 5:66-67. Like dialkylamides, many of these compounds are also highly reactive and thermally stable (e.g., trialkyls of Al, Ga and In; dialkyls of Zn, Cd and Hg, anhydrous metal nitrates (e.g., $\text{Ti}(\text{NO}_3)_4$), amine alanes $[(\text{R}_3\text{N})\text{AlH}_3]$, metal chlorides (e.g., TiCl_4), and many others). A person of ordinary skill in the art would not rely on these characteristics to specifically identify metal dialkylamides as suitable for an ALD process to produce a metal oxide film.

96. Further, while reactivity, volatility, and thermal stability are beneficial for use in an ALD process, they do not provide any definitive indication that a specific compound would be suitable for an ALD process to produce a metal oxide film. Buchanan discloses tens of thousands of precursor mixtures with no teaching or suggestion that amino-containing precursors would be suitable for use in an ALD process to form a metal oxide film. In fact, given that the only disclosure in Buchanan for forming a metal oxide film via an ALD process involves the use of zirconium nitrate and hafnium tertbutoxide, one of ordinary skill in the art would have been led to use such metal-ligand compounds, rather than amino-containing precursors, for forming metal oxide films using an ALD process.

97. Petitioner further argues that a person of ordinary skill in the art would modify Example 3 to use alkylamides because Buchanan describes both nitrates and alkoxides as having suboptimal chemical characteristics. See '663 Petition at 50 (citing Ex. 1005 at 2:23-44). Buchanan, however, describes that alkylamides have the same suboptimal chemical characteristics as alkoxides. Particularly, Buchanan states that similar to alkoxides, amides are “prone to ligand rearrangement, hydrolysis, oxidation, oligomerization, ring formation and existing in several interconvertible isomeric forms resulting in irreproducible vapor pressures over time.” Ex. 1005 at 2:45-49. As such, in my opinion, a person of ordinary skill in the art would not replace the alkoxide precursor in Example 3 (tertbutoxide) with an amine-containing precursor because Buchanan discloses that amides are prone to similar problems associated with alkoxides.

98. Additionally, the Petitioner argues that it would have been obvious to a person of ordinary skill in the art to try metal dialkylamides in Buchanan's Example 3 because “Buchanan refers in Example 3 generally to “Zr-containing” and “Hf-containing” precursors. See '663 Petition at 51. I disagree. As discussed below in Section VI.A.2.a(2), a person of ordinary skill in the art would understand that precursor chemistry is unpredictable and that the zirconium nitrate and hafnium tertbutoxide precursors used in Example 3 could not be replaced with other precursor compounds with any reasonable degree of confidence that the ALD

process would be successful. Additionally, Example 3 makes no mention of metal dialkylamides. A person of ordinary skill in the art considering Example 3 would have no motivation to look to metal dialkylamides.

99. In my opinion, if a person of ordinary skill in the art were to consider modifying Buchanan's Example 3, the person would first consider the ligand group attached to each metal element, rather than considering the metal element itself. Example 3 specifically discloses using zirconium nitrate and hafnium tertbutoxide precursors. Ex. 1005 at 19:60-20:24. Buchanan dedicates specific sections of its disclosure to "Precursor Source Mixtures for Nitrate-Containing Compound" (e.g., zirconium nitrate), and "Precursor Source Mixtures for Alkoxy-Containing Compound" (e.g., hafnium tertbutoxide). *Id.* at 13:4-14:2, 16:1-55. As such, in view of Buchanan's disclosure, a person of ordinary skill in the art considering modifying Buchanan's Example 3 would first look to nitrate and alkoxide precursor compounds.

100. Further, a person of ordinary skill in the art would have no motivation to replace the zirconium nitrate and hafnium tertbutoxide precursors used in Example 3 with a dialkylamide. As discussed above, Buchanan discloses that amides are prone to similar problems as alkoxides. Ex. 1005 at 2:45-49. A person of ordinary skill in the art would have no reason to replace an alkoxide with an amide compound with similar problems. Additionally, a person of ordinary skill in

the art would have no reason to replace the zirconium nitrate precursor with a dialkylamide because nitrates and dialkylamides are compounds with significantly different chemical properties and would not be considered interchangeable, as discussed below.

101. Zirconium nitrate ($\text{Zr}(\text{NO}_3)_4$) is in the class of metal complexes known as anhydrous metal nitrates. Anhydrous metal nitrates are powerful oxidizing agents in which the nitrogen exists in its highest (+5) oxidation state surrounded by three oxygens. In $\text{Zr}(\text{NO}_3)_4$, there is no direct bond between the nitrogen and the metal. On the other hand, a zirconium dialkylamido compound ($\text{Zr}(\text{NR}_2)_4$) is not an oxidant. The nitrogen is present in its lowest (-3) oxidation state and there is a direct bond between the nitrogen and the metal. Additionally, nitrate ligands are labile and can be easily substituted by other, especially anionic, ligands, whereas dialkylamido ligands are less labile than the nitrates and simple substitutions are less favorable. A person of ordinary skill in the art would be aware of these, and other, differences between nitrates and dialkylamides and would not consider them to be interchangeable.

102. I note that if one of ordinary skill in the art were to look to the claims of the Buchanan patent, which I understand embody the patentable contributions of Buchanan to the art, such a person would not find any amido-containing metal precursors listed in the claims.

103. Finally, Petitioner argues Buchanan discloses a “self-limiting” ALD process using a metal alkylamide precursor to form a metal oxide because the process in Example 3 is self-limiting because it is an ALD process and because its disclosed growth per cycle indicates that it either is or can be made to be self-limiting. *See* ’663 Petition at 3. I disagree.

104. In my opinion, a person of ordinary skill in the art would not have found Example 3 to disclose or render obvious the use of a metal alkylamide precursor in a self-limiting process to produce a metal oxide film. Example 3 provides no teaching or suggestion that it can be modified to arrive at a self-limiting ALD process using any other precursor. *See* Ex. 1005 at 19:60-20:49. As discussed above, Buchanan does not teach or suggest modifying Example 3 to use a metal alkylamide precursor. Buchanan also does not teach or suggest that a metal alkylamide precursor can be used in Example 3 in a self-limiting manner.

105. As discussed more fully below, the ability to run an ALD process in a self-limiting manner depends on the precursors and reactants chosen for the process and the specific process conditions at which the process is run. A person of ordinary skill in the art would understand that each self-limiting ALD process will require unique processing conditions to run in a self-limiting manner based on the choice of precursor(s) and reactant(s). Further, a person of ordinary skill in the art would understand that in some cases no self-limiting ALD process can be

achieved. As such, a person of ordinary skill in the art would not have been motivated to modify Buchanan's Example 3 to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film.

(2) Buchanan fails to teach a viable ALD process for each of the vast amount of metal precursors disclosed

106. A person of ordinary skill in the art would have understood that the focus of Buchanan is on the use of a solvent to form precursor source mixtures. Buchanan's precursor mixtures are composed of a metal, which is bound to at least one ligand, dissolved, emulsified, or suspended in an inert organic liquid. *Id.* at Abstract, 3:56-4:21. A person of ordinary skill in the art would have known that not all of Buchanan's disclosed precursors are suitable for both CVD and ALD processes. And based on Buchanan's disclosure, a person of ordinary skill in the art would have no reasonable expectation that metal dialkylamides could be used in an ALD process to produce metal oxide film.

107. Petitioner argues that based on Buchanan's teachings, each-and-every one of its precursors is suitable for use in both CVD and ALD processes because Buchanan states that its precursors can be used in any CVD or ALD process. *See* '663 Petition at 49. In my opinion, Petitioner's arguments and interpretation of Buchanan are inconsistent with what was known by those of ordinary skill in the art.

108. To accept Petitioner's interpretation of Buchanan, a person of ordinary skill in the art would have to believe that Buchanan discloses that tens of thousands of precursor mixtures are suitable for use in both CVD and ALD processes. As discussed above, Buchanan's precursor mixtures are composed of one of fifty (50) elements and at least one ligand selected from twenty (20) ligand groups, in one, or a mixture of inert liquids selected from twenty-one (21) groups of inert liquids. See Ex. 1005 at Abstract. Buchanan's identification of so many elements, groups of ligands, and inert liquids with the additional mixture options leads to tens of thousands of precursor mixtures.

109. A person of ordinary skill in the art would not have interpreted Buchanan as alleged by Petitioner. A person of ordinary skill in the art would know that precursor chemistry leads to unpredictability with regard to which precursors work with CVD and/or ALD, and also would have known that certain precursors, including those identified as "preferred precursors" in Buchanan, are not suitable for both CVD and ALD, as discussed in more detail below.

(a) Precursor chemistry is unpredictable

110. A person of ordinary skill in the art would understand that the chemistry involved in the formation of a metal film via an ALD process using precursors is unpredictable. For example, Petitioner's own cited references acknowledge the difficulties with developing suitable ALD processes and the

associated precursors. *See, e.g.*, Ex. 1044, Goodman at 8 (“although the general conditions under which [ALD] would be possible seem reasonable [sic] clear, each material will have its own specific requirements regarding the operational conditions under which deposits of high perfection and purity could be obtained- while in some cases [ALD] might turn out not to be applicable.”).

111. In the late 1990s, at the time of the invention, those of skill in the art understood that it was difficult to predict without extensive experimentation whether a precursor could be used in an ALD reaction to form a desired film. For example, those of ordinary skill recognized that while thermodynamic considerations of the reactions prior to experimental work are useful, thermodynamic considerations alone cannot be used to predict with any reasonable degree of confidence whether film growth will occur. Ex. 1008, Leskelä I at 20. Rather, extensive experimentation would be required to determine whether suitable film growth would occur.

112. Additionally, a person of ordinary skill in the art would have known that to improve process control and to assist in designing new ALD processes, in situ monitoring of known reactions would be needed to gain an understanding of ALD growth reactions. *See* Ex. 1008 at 27; Ex. 1012, George at 14 (commenting that surface chemistry studies are essential to understanding and controlling complex ALD reactions).

113. In the late 1990s, those of skill in the art understood the importance of and difficulties with precursor chemistry in ALD processes and understood that further development and testing was necessary.

There are a lot of challenges and development work to be done before ALD is accepted as an important thin film deposition technology for opto- and microelectronics. As pointed out above the key role in the process development is the precursor chemistry. The first challenge is to get more chemists to work with the precursors. CVD faces the same challenge because worldwide the precursor development is not very extensive. On the other hand, there are of course more companies specializing on CVD precursors than ALD precursors. Luckily, these companies have shown increasing interest towards [] ALD which is a natural development recognizing the similarities of the two fields.

Ex. 1013, Leskelä II at 21.

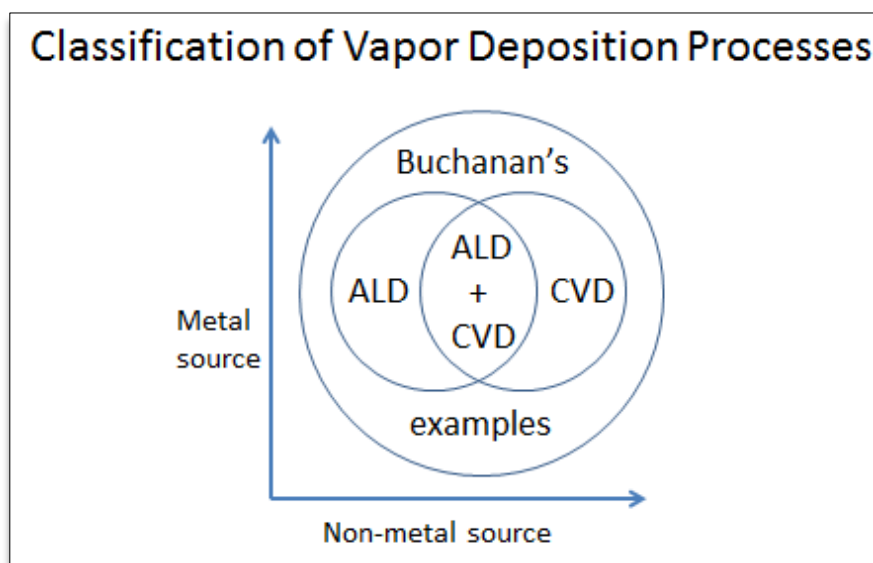
114. Given the unpredictable nature of ALD and CVD processes, one of ordinary skill in the art would not have been able to determine with any reasonable degree of confidence which of the myriad precursor mixtures disclosed in Buchanan would have been suitable for use in an ALD process to form an oxide film, without extensive experimentation.

(b) Not all precursors disclosed in Buchanan are suitable for both CVD and ALD

115. In my opinion, Petitioner's interpretation of Buchanan's teachings improperly assumes that each-and-every precursor mixture disclosed in Buchanan

is suitable for both ALD and CVD. See '663 Petition at 49 (interpreting Buchanan as disclosing that each-and-every one of its precursors is viable for use in both CVD and ALD processes). A person of ordinary skill in the art would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD.

116. The diagram below visually depicts that not all precursors disclosed in Buchanan are suitable for use in both an ALD and a CVD process. And, in some cases, disclosed precursors are not suitable for either ALD or CVD. For example, bis(benzene)cobalt that is listed as a preferred precursor in Buchanan (Ex. 1005 at 6:17) is not suitable for use in a CVD process or an ALD process. Bis(benzene)cobalt has never been isolated as a pure compound. It is thermally stable only up to -3°C, and hence it is unsuitable for both CVD and ALD processes. Ex. 2110, Bechamp.



117. In another example, Buchanan discloses as “preferred precursors” tetramethyl-, tetraethyl-, tetraphenyl-, or tetra-n-butyl-Si (Ex. 1005 at 6:7-8). Although volatile, these are remarkable stable compounds. Tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, is a known CVD precursor for deposition of silicon carbide (SiC), but depositions are conducted at temperatures greater than 900°C . Ex. 2109, Herlin. The thermal stability and lack of reactivity of tetramethylsilane render it useless as an ALD precursor. The thermal stability and lack of reactivity of tetramethylsilane is so great that it was chosen decades ago to be the standard reference compound in Nuclear Magnetic Resonance (NMR) spectroscopy. Ex. 2111, Tiers. This spectroscopy is used by people who prepare and characterize precursors for use in CVD and ALD. A person of ordinary skill in the art would know that these alkylsilane “preferred precursors” would not work with ALD because they do not chemisorb onto surfaces, which is a process required for ALD.

118. Buchanan also discloses as “preferred precursors” $(\text{Me}_3\text{N})\text{AlH}_3$; $(\text{EtMe}_2\text{N})\text{AlH}_3$; $(\text{Et}_3\text{N})\text{AlH}_3$; bisethylbenzene- or bisbenzene-Co, Mo or Cr; ethylferrocene; $\text{Ru}_3\text{CO}_{12}$; $\text{Fe}(\text{CO})_5$; $\text{Co}_2(\text{CO})_8$; $\text{Ru}(\text{CO})_3(1,3\text{-cyclohexadiene})$; $\text{Os}_3\text{CO}_{12}$; $\text{Cr}(\text{CO})_6$; $\text{CpCo}(\text{CO})_2$; $\text{Mn}_2(\text{CO})_{10}$; $\text{Mo}(\text{CO})_6$; $\text{Ni}(\text{CO})_4$; $\text{Re}_2(\text{CO})_{10}$; $\text{Ru}_3\text{CO}_{12}$; $\text{W}(\text{CO})_6$; $((\text{CH}_3)_3\text{SiO})_4\text{Si}$; (tert-butoxy) CuPMe_3 ; $\text{Pt}(\text{PF}_3)_4$; $\text{Ni}(\text{PF}_3)_4$; $\text{Cr}(\text{PF}_3)_6$; $\text{Ir}(\text{PF}_3)_4$. See Ex. 1005 at 6:3-60. These precursors deposit material by thermal decomposition. This decomposition process is not self-limiting, so these precursors would not work in ALD, which requires self-limiting reactivity with a surface.

119. There are significant differences between CVD and ALD processes, and hence precursors that may be suitable for a CVD process are not necessarily suitable for use in an ALD process. In fact, in 2006, a study concluded that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD. See Ex. 2102. The study recognized that new high-K dielectric oxide films such as Al_2O_3 , ZrO_2 , HfO_2 , Zr and Hf silicate, $(\text{HfO}_2)_x(\text{Al}^2\text{O}_3)_{1-x}$, La_2O_3 , Pr_2O_3 , Y_2O_3 , Gd_2O_3 , and Nd_2O_3 , were under research to replace SiO_2 films due to problems with SiO_2 regarding direct electron tunneling and high leakage current. *Id.* at Abstract, 1. The study focused on the use of “metal alkoxide precursors, containing bidentate donor-functionalized alkoxide ligands” in CVD and ALD. Ultimately, the study concluded that such

precursors markedly improved the CVD process, but were not suitable for ALD.

Id. at Abstract, 14. The authors noted that the findings “highlight[ed] the very different requirements of MOCVD and ALD precursors.” *Id.* at Abstract.

120. As an additional example, commercial copper precursor CupraSelect® is found to be suitable for CVD processes but to not be suitable for ALD processes. The CupraSelect® molecule is optimized with a weak bond that provides the key to growing a pure copper film by CVD. “The problem [with CupraSelect] is that the original compound undergoes facile disproportionation, a reaction highly desirable for the CVD of metallic copper films, but which limits its use for ALD applications.” Ex. 2113, Zaera. Though suitable for CVD, the instability of CupraSelect® renders it unsuitable for ALD.

121. Further a person of ordinary skill in the art would understand that suitability of a precursor for use in any of a CVD or an ALD process is not necessarily indicative of its suitability in the other process. For example, Buchanan identifies the “preferred precursors” trimethyl-, triethyl-, triisobutyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or ethyldimethyl-B, Al, Ga, In, As or Sb. Ex. 1005 at 6:4-6. The chemical trimethylaluminum (TMA) is well-known to function in an ALD reaction with water vapor to deposit films of aluminum oxide. However, TMA cannot be used in a CVD process with water to deposit films of aluminum oxide. Mixing TMA vapor with water vapor in a

hypothetical CVD process will produce powder dispersed in the gas phase by a fast homogeneous reaction in the gas phase, but no film will be deposited on any surface.

(3) A person of ordinary skill in the art would have been dissuaded from using metal dialkylamides in an ALD process to form a metal oxide film

122. In my opinion, one of ordinary skill in the art would have been disinclined to use metal dialkylamides for forming a metal oxide film using an ALD process. This is so because one of ordinary skill in the art would have expected the metal oxide films produced by an ALD process using a metal dialkylamide to be contaminated with unsuitably high concentrations of carbon and nitrogen impurities.

123. By the 1970s, CVD was already a widely-used method for preparing films for many applications. Depositions of films consisting of two different elements (e.g., SiO_2 , GaAs, SnO_2 , InP, AlN, etc.) required the use of two separate gaseous precursors (one for each of the elements). Film stoichiometry (i.e., elemental ratios) had to be controlled by separate precursor delivery systems. A surge of interest in precursor design focused on molecules that could act as a single source precursor for single source CVD. The hypothesis was that deposition chemistry could be used to control film stoichiometry. In addition to the usual precursor requirements including volatility (liquids and gases are preferred over

solids), stability (e.g., long shelf life), and safety (avoid pyrophoric, explosive, and highly toxic precursors), single source precursor design was considered to be governed by the following principles: 1) the use of molecules having the two elements bonded directly to one another preferably in the ratio required by the desired film stoichiometry; and 2) the use of molecules that have an efficient route for cleaving the unwanted ligands that were necessary to provide precursor volatility and stability.

124. Single source CVD is similar to ALD in the way that precursors interact with a heated substrate in a deposition chamber. In single source CVD, a single precursor is introduced into the deposition chamber, usually with a carrier gas, to form a film on a heated substrate. Similarly, in ALD, precursors are alternately introduced into the deposition chamber, such that only a single precursor is introduced into the deposition chamber at a time.

125. Metal dialkylamides were considered for use as a single source precursor for single source CVD because they were thought to possess the necessary characteristics. See Ex. 2114, Sugiyama. For example, with four nitrogen atoms bound directly to the metal, at first glance the metal dialkylamide tetrakis(dimethylamido)titanium, $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$, would appear to be an attractive single source precursor for the formation of titanium nitride, TiN. However, the early work on this and related dialkylamido metal complexes revealed that

chemical vapor deposited films had an unacceptable amount of carbon contamination, upwards of 50% by atomic weight of the deposited film. *See* Ex. 2103. The early results using single source metal dialkylamides suggested that there did not appear to be an efficient route for cleaving the C-N bonds of the dialkylamido ligands.

126. As such, a person of ordinary skill in the art would have known that the use of dialkylamido metal complexes in a single source CVD process results in deposition of unacceptable levels of carbon impurities in the resulting film. *See* Ex. 2103; Ex. 2104; Ex. 2105; Ex. 2106.

127. In the 1990s, further research regarding the use of metal dialkylamides for use in CVD was performed. For example, a series of mechanistic studies of the CVD of TiN using $\text{Ti}(\text{NMe}_2)_4$ were published by Dubois, et. al., from Bell Labs in 1992 and 1994. *See* Ex. 2105; Ex. 2106. These studies recognized the issues with carbon contamination in single source CVD. For example, Dubois '94 indicated that "since titanium and nitrogen are bonded directly in $[\text{Ti}(\text{NMe}_2)_4]$, one might expect the pyrolysis of this material to lead to the formation of TiN thin films. Ex. 2016 at 2. Previous studies have shown that this is indeed the case, however, as noted above, the films are contaminated with carbon." Dubois '94, however, reported that suitable films, with low carbon

content could be obtained if the CVD process was run with ammonia (NH_3) along with the metal dialkylamide precursor.

128. In my opinion, based on what was known about CVD using metal dialkylamides, a person of ordinary skill in the art would have been dissuaded from using them in an ALD process to produce a metal oxide film.

129. First, in my opinion, a person of ordinary skill in the art would have considered that the use of metal dialkylamides in ALD would be similar to their use as a single source precursor in CVD. In an ALD process involving a metal dialkylamide precursor such as $\text{Ti}(\text{NMe}_2)_4$, a heated surface would be exposed to only the dialkylamide precursor from the moment that the dialkylamide precursor pulse begins until it ends (typically several seconds) and including the time required for a purge pulse (typically several more seconds). During such a period, the precursor will be adsorbed on the heated surface and would be expected to react in the same fashion as that observed in a single source CVD process using only that precursor, i.e., depositing a large percentage of carbon as an unwanted impurity in the growing film. Hence, a person of ordinary skill in the art would have been disinclined to consider using metal dialkylamide precursors in an ALD process to deposit a metal oxide film because such a person would have been concerned about carbon contamination in the resulting film. In particular, such carbon contamination can increase the electrical leakage and decrease the

breakdown field of an oxide insulator, which are undesirable in many applications (e.g., DRAM).

130. Second, a person of ordinary skill in the art would understand that if one were to use a metal dialkylamide for depositing a metal oxide film, as opposed to a metal nitride film, not only carbon but also nitrogen would be a source of contamination in the resulting film. Further, a person of ordinary skill in the art would know that ammonia (NH_3), which was employed in the Dubois '94 to reduce carbon contamination, would not be a suitable reactant for the formation of an oxide film.

131. Third, in my opinion, a person of ordinary skill in the art would be further concerned with carbon contamination due to Buchanan's required organic solvent. Buchanan teaches that all of its precursors are dissolved in an inert organic solvent. Ex. 1005 at Abstract, 3:56-4:21. A person of ordinary skill in the art would understand that the introduction of an organic solvent into the deposition chamber could result in more complex chemical reactions. A person of ordinary skill in the art would understand that the organic solvent would provide an additional source of carbon that could become integrated into a growing film, resulting in additional unwanted carbon impurities. Buchanan identifies that the inert organic solvent should be selected such that it would not incorporate such impurities. Ex. 1005 at 7:20-25. However, Buchanan provides no guidance

regarding how to identify such a solvent. A person of ordinary skill in the art would not be able to determine which inert organic solvent would be suitable without extensive experimentation. Moreover, some solvents are flammable, increasing the possibility of fire or event explosion. Further, some solvents are toxic and/or carcinogenic. The use of a solvent can also add cost to the process. And additional expensive equipment would be needed to remove solvent vapor from the exhaust gases before releasing the carrier gas (typically nitrogen) into the environment.

(4) A person of ordinary skill in the art would not have combined the teachings of Buchanan and Min to arrive at the process of Claim 1

132. Petitioner argues that it would have been obvious to a person of ordinary skill in the art to modify Buchanan's Example 3 based on Min to arrive at a self-limiting ALD process using a metal dialkylamide to form a metal oxide film. See '663 Petition at 36, 38, 48-58. Petitioner also argues that a person of ordinary skill in the art would have modified Min's ALD process based on Buchanan to arrive at an ALD process using a metal dialkylamide to form a metal oxide film. *Id.* at 38-39. I disagree with Petitioner's conclusions.

133. First, I note that the Petitioner does not appear to allege any motivation to combine the teachings of Buchanan and Min to modify Min's ALD process to use a metal dialkylamide to form a metal oxide film. Rather, Petitioner

only addresses the modification of Buchanan's Example 3 in view of Min to achieve a self-limiting ALD process. See '663 Petition at 53-59 (Section 10.9.2, Motivations to Combine Buchanan and Min). However, my opinions below apply generally to the combination of Buchanan and Min and are not limited to a specific modification.

134. In my opinion, a person of ordinary skill in the art would have had no motivation to combine the teachings of Buchanan and Min to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film. Neither Buchanan nor Min discloses a self-limiting ALD process using a metal alkylamide to form a metal oxide film and a person of ordinary skill in the art would not have been motivated to modify the teachings of Buchanan and Min to arrive at such a process.

135. The Petitioner argues that to the extent Buchanan does not disclose a self-limiting process, it would have been obvious to combine Buchanan's ALD process in Example 3 with the self-limiting process taught by Min. '663 Petition at 53-54. The Petitioner argues that Buchanan provides express motivation for this modification to Example 3 because Buchanan "expressly states that as semiconductor devices have been decreasing in size, there has arisen an acute need to precisely control film thickness" and because it was known that self-limiting ALD could precisely control film growth. See *id.* (quoting Ex. 1005 at 1:15-27). I

disagree. In my opinion, a person of ordinary skill in the art would not have interpreted Buchanan to motivate that its disclosed process required modification.

136. A person of ordinary skill in the art would understand that Buchanan is directed to “a precursor source mixture useful for CVD and ALD applications, methods of growing films (as well as layers, coatings and multilayers) utilizing the precursor source mixture of the present invention, and methods of fabricating electronic devices incorporating a film deposited by the inventive method.” Ex. 1005 at 3:56-66. Buchanan simply points out the shortcomings of prior art systems for the delivery of precursors to a CVD or an ALD reactor, and provides a solution for many of these shortcomings, i.e., the use of a solvent. *See* ’663 Petition at 53-54 (citing Ex. 1005 at 1:15-27). Further, such a disclosure offers no teaching or suggestion to a person of ordinary skill in the art to modify Example 3 to use a metal alkylamide in a self-limiting ALD process to produce a metal oxide film.

137. The Petitioner also argues that a person of ordinary skill in the art would have modified Buchanan’s Example 3 in view of Min’s self-limiting ALD process because it was known in the art that optimizing process conditions can lead to self-limiting processes. *See id.* at 54-55. The Petitioner argues that “the results of combining Buchanan’s ALD method with self-limiting ALD deposition processes as taught in Min would have been predictable, routine to achieve, and

understood to yield predictable results.” *Id.* at 55. However, in my opinion, the Petitioner mischaracterizes the state of the art and Min’s discloses ALD process.

138. In my opinion, Min’s teachings are limited to the use of ALD for forming TiN films and one of ordinary skill in the art would not have a reasonable expectation that those teachings could be successfully generalized to other systems, such as that proposed by the Petitioner.

139. For example, the data presented in Min’s FIG. 3 shows that the “ALD window” for Min’s process is limited to a narrow temperature window, i.e., between 170°C to 210°C, in which the TiN film growth is self-limiting. The ALD window depends not only on the properties of the precursor but also those of the reactant. Min indicates that TiN films “are not deposited below 150°C, indicating that reactant sources are mainly physisorbed on the surface below 150°C.” Min explains that “[c]hemisorption involves the formation of relatively strong chemical bonds whereas in physisorption, the effective forces are of weak van der Waals type. Thus, weak bonds of physisorption can be easily purged by Ar.” *Id.* at 8. Min further explains that above 230 C, the deposition process transitions from an ALD process to an MOCVD process, which is not self-limiting. *Id.*

140. It is not, however, possible to predict with any reasonable degree of confidence whether changing any of the precursor or the reactant of an ALD system would result in a system for which an ALD window would be available.

For example, a change of the reactant may result in a system in which the chemisorption of the reactant would occur at such elevated temperatures at which the precursor would not be thermally stable. In fact, as discussed above, precursor-reactant systems are known that can be successfully used in a CVD process, but not in an ALD process because of the lack of a suitable ALD window (e.g., Tetramethylsilane, $\text{Si}(\text{CH}_3)_4$). One of ordinary skill in the art would not have been able to predict with any reasonable degree of confidence whether Buchanan's Example 3 could be modified to result in a process for which an ALD window would be available.

141. Further, in my opinion, a person of ordinary skill in the art would not have been motivated to combine Buchanan and Min to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film due to the unpredictable nature of ALD processes. As discussed above in VI.A.2.a(2), Petitioner's own cited references reveal difficulties in predicting whether a precursor would be suitable for use in an ALD process. *See, e.g.*, Ex. 1044 at 8 ("although the general conditions under which [ALD] would be possible seem reasonable [sic] clear, each material will have its own specific requirements regarding the operational conditions under which deposits of high perfection and purity could be obtained-while in some cases [ALD] might turn out not to be applicable.").

142. Additionally, a person of ordinary skill in the art would have recognized that Min discloses a highly specific ALD process limited to the formation of TiN films. Particularly, a person of ordinary skill in the art would have recognized that Min is directed to the specific investigation of ALD using TEMAT and NH_3 to produce TiN films on SiO_2 . Ex. 1006 at Abstract. A person of ordinary skill in the art would have known that Min's specific teachings are not transferrable to all ALD processes. For example, Min identifies that its ALD process is not typical of other ALD processes because it deposited films with a thickness of 1.6ML/cycle. See Ex. 1006 at 10 ("As shown in Fig. 7, saturated film thickness per cycle is 0.6 nm/cycle, which corresponds to 1.6 ML/cycle. However, it has previously been reported that film thickness per cycle of the ALD process is limited to below 1 ML/cycle.").

143. Further, a person of ordinary skill in the art would have understood that Min's results are based on the specific reactants chosen for its ALD process, i.e., TEMAT and NH_3 . Min found that its ALD process using TEMAT and NH_3 was required to operate in the temperature range between 170°C and 210°C, based on its chosen reactants. *Id.* at 8. Min also found that the carbon contamination in the resulting film was also dependent on its chosen reactants. *Id.* at 10. Specifically, Min found that the use of NH_3 was required to reduce the carbon contamination in the deposited nitride film. See *id.*

144. A person of ordinary skill in the art would recognize that Min provides no teachings with respect to other reactants. Further, Min provides no teaching with respect to the deposition of films other than nitride films, such as oxides. In view of Min, a person of ordinary skill in the art would have no reasonable expectation that a self-limiting ALD process using metal dialkylamides would successfully result in the deposition of a metal oxide film.

145. Further, a person of ordinary skill in the art would have understood that modifying Min's ALD process to form an oxide film, rather than a nitride film that is the focus of Min's teachings, can pose a number of difficulties. For example, a person of ordinary skill would understand that using a metal dialkylamide precursor to form a metal oxide involves the high possibility of the introduction of both carbon and nitrogen as impurities into the growing oxide film. A person of ordinary skill in the art would further recognize that the alternate introduction of a metal dialkylamide precursor and an oxidizing agent, as in ALD, onto a substrate would likely increase that possibility. The alternate introduction of a metal dialkylamide precursor and an oxidizing agent, onto a substrate would result in the adsorption of at least part of the precursor on the substrate and its presence on the substrate surface by itself for a period of time prior to the introduction of the oxidizing agent. During such a period, carbon and nitrogen of the precursor could be incorporated into the growing film.

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

147. A person of ordinary skill in the art would have understood that Min's use of ammonia as a reactant reduces carbon impurities. Ammonia, however, cannot be used a reactant to provide the oxygen source necessary to form a metal oxide film. As such, one of ordinary skill would understand that the teachings of Min regarding the formation of a TiN film is not simply transferrable to the formation of a metal oxide film.

b. The Combination of Buchanan and Min Fails to Disclose or Render Obvious Claims 2-3, 5-7, 9-10 of the '016 Patent.

(1) Claim 2: The process as in Claim 1, wherein the insulator insulates a gate or a capacitor.

148. In my opinion, the combination of Buchanan and Min fails to disclose Claim 2 of the '016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claim 1. Further, the combination of

Buchanan and Min fails to disclose the additional limitation that “the insulator insulates a gate or a capacitor.”

149. In arguing that the combination of Buchanan and Min discloses the process in Claim 1, Petition relies almost exclusively on Buchanan’s Example 3. See ’663 Petition at 32-41. With regard to Claim 2, Petition argues that the process of Claim 1 with the additional limitation that “the insulator insulates a gate or a capacitor” is taught or rendered obvious by Buchanan’s Examples 12 and 15. See *id.* at 41-42.

150. Buchanan does not disclose, or suggest, a self-limiting ALD process using a dialkylamide precursor to form a metal oxide film, wherein the metal oxide film insulates a gate or a capacitor, as recited by Claim 2. Buchanan’s Examples 12 and 15 make no mention of a self-limiting ALD process using a metal dialkylamide processor. See Ex. 1005 at 23:55-24:55; 26:17-27:15. Further, nothing in Buchanan would lead a person of ordinary skill in the art to modify these examples to use such a process to insulate a gate or a capacitor.

(2) Claim 3: The process in Claim 2, wherein the metal alkylamide is a hafnium dialkylamide.

151. In my opinion, the combination of Buchanan and Min fails to disclose Claim 3 of the ’016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1 and 2. Further, the combination of

Buchanan and Min fails to disclose the additional limitation that “the metal alkylamide is a hafnium dialkylamide.”

152. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 3 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1 and 2, I disagree. In particular, as discussed above, Buchanan does not teach, or suggest, using a metal alkylamide in an ALD process to form an oxide film, much less using a specific metal alkylamide, such as hafnium dialkylamide.

(3) Claim 5: The process as in Claim 3, wherein the hafnium dialkylamide is tetrakis(dimethylamido)hafnium.

153. In my opinion, the combination of Buchanan and Min fails to disclose Claim 5 of the ’016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1-3. Further, the combination of Buchanan and Min fails to disclose the additional limitation that “the hafnium dialkylamide is tetrakis(dimethylamido)hafnium.”

154. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 5 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1-3, I disagree.

(4) Claim 6: A process as in Claim 3, wherein the hafnium dialkylamide is tetrakis(diethylamido)hafnium.

155. In my opinion, the combination of Buchanan and Min fails to disclose Claim 6 of the '016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1-3. Further, the combination of Buchanan and Min fails to disclose the additional limitation that “the hafnium dialkylamide is tetrakis(diethylamido)hafnium.”

156. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 6 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1-3, I disagree.

(5) Claim 7: A process as in Claim 2, wherein the metal alkylamide is a zirconium dialkylamide.

157. In my opinion, the combination of Buchanan and Min fails to disclose Claim 7 of the '016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1 and 2. Further, the combination of Buchanan and Min fails to disclose the additional limitation that “metal alkylamide is a zirconium dialkylamide.”

158. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 7 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1 and 2, I disagree.

(6) Claim 9: A process as in Claim 7, wherein the zirconium dialkylamide is tetrakis(dimethylamido)zirconium.

159. In my opinion, the combination of Buchanan and Min fails to disclose Claim 9 of the '016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1, 2, and 7. Further, the combination of Buchanan and Min fails to disclose the additional limitation that “the zirconium dialkylamide is tetrakis(dimethylamido)zirconium.”

160. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 9 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1, 2, and 7, I disagree.

(7) Claim 10: A process as in Claim 7, wherein the zirconium dialkylamide is tetrakis(diethylamido)zirconium.

161. In my opinion, the combination of Buchanan and Min fails to disclose Claim 10 of the '016 Patent. As discussed above, the combination of Buchanan and Min fails to disclose the process as in Claims 1, 2, and 7. Further, the combination of Buchanan and Min fails to disclose the additional limitation that “the zirconium dialkylamide is tetrakis(dimethylamido)zirconium.”

162. Petitioner argues that to the extent Buchanan does not expressly disclose Claim 10 it would have been obvious in view of Buchanan’s Example 3. For the same reasons as discussed above with respect to Claims 1, 2, and 7, I disagree.

B. Grounds Based on Buchanan, Min, and Shin

163. It is my understanding that the Petitioner has alleged that Buchanan in view of Min and Shin renders obvious Claim 8 of the '016 Patent. '663 Petition at 4. Having reviewed, among other things, Buchanan, Min, Shin, the '663 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Buchanan in view of Min, and Shin as presented by the Petitioner, does not render obvious Claim 8 of the '016 Patent.

1. Summary of Korean Patent KR0156980 "Compound for the Deposition of Metal Nitride Thin Film and Deposition Method Thereof" ("Shin")

164. Shin is directed to a precursor compound used to deposit metal nitride thin film over a silicon substrate. Ex. 1007 at 1. Shin is further directed to a titanium nitride (TiN) film deposition process using a chemical vapor deposition process. *Id.* at 6. Shin contains no mention of an ALD process. See Ex. 1007. Further, Shin was disclosed during the examination process of the '016 Patent and is listed on the face of the patent. Ex. 1001.

2. A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Buchanan, Min, and Shin

165. In my opinion, a person of ordinary skill in the art would have no motivation to combine the teachings of Shin with Buchanan and Min. Shin is directed to a compound for the deposition of a metal nitride film over a silicon substrate. Shin makes no mention of using a metal alkylamide in a self-limiting

ALD process to produce a metal oxide film, as recited by Claim 8. A person of ordinary skill in the art would have had no reason to look to Shin to combine with and modify the teachings of Buchanan and Min.

166. The Petitioner argues that a person of ordinary skill in the art would have been motivated to combine the teachings of Buchanan and Min, with Shin to use tetrakis(ethylmethyldamino) zirconium as a metal alkylamide precursor in a self-limiting ALD process to form a metal oxide film. See '663 Petitioner at 61-62. Particularly, the Petitioner argues that a person of ordinary skill in the art would have been motivated to use tetrakis(ethylmethyldamino) zirconium because Buchanan discloses the general formula for a genus to which tetrakis(ethylmethyldamino) zirconium belongs and Buchanan teaches that tetrakis(dimethyldamino) zirconium and tetrakis(diethyldamino) zirconium are “highly preferred” precursors. See *id.* at 62-64. The Petitioner also argues that “Shin teaches that such a compound may ‘neutralize[]’ shortcomings of its – dimethyldamino and –diethyldamino variants” and that its use in an ALD process to produce a metal oxide film would have been obvious to try and would have had a reasonable expectation of success. See *id.* at 64-66. For the following reasons, I disagree.

167. As discussed above, Buchanan discloses tens of thousands of precursors. Buchanan also discloses a myriad of precursors which Buchanan

designates as “preferred precursors” and certain additional precursors as “highly preferred.” Buchanan, however, does not disclose tetrakis(ethylmethyamino) zirconium. In my opinion, one of ordinary skill in the art would find no teachings or suggestion in Buchanan that this compound would be suitable for use in an ALD process to deposit an oxide film. In fact, as discussed above, Buchanan provides no teaching that its preferred or highly preferred precursors, including any disclosed metal alkylamide, are suitable for use in a self-limiting ALD process to form a metal oxide film.

168. Additionally, a person of ordinary skill in the art would not have been motivated to use tetrakis(ethylmethyamino) zirconium in an attempt to ““neutralize[]’ shortcomings of its –dimethylamino and –diethylamino variants,” as alleged by the Petitioner. *Id.* at 64. Buchanan makes no mention of tetrakis(ethylmethyamino) zirconium and does not describe any shortcomings associated with “its –dimethylamino and –diethylamino variants.” A person of ordinary skill in the art presented with Buchanan would have had no motivation to solve a problem that was not known to exist.

169. Further, for all the reasons discussed above, a person of ordinary skill in the art would have no motivation to try tetrakis(ethylmethyamino) zirconium and would not have known with any reasonable degree of confidence whether it

could be successfully used in a self-limiting ALD process to produce a metal oxide film.

VII. OPINIONS ON IPR2017-00664

A. Grounds Based On Senzaki and Min

170. It is my understanding that the Petitioner has alleged that Senzaki in view of Min renders obvious Claims 1, 2, 7, and 10 of the '016 Patent. '664 Petition at 4. Having reviewed, among other things, Senzaki, Min, the '664 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Senzaki in view of Min, as presented by the Petitioner, does not render obvious Claims 1, 2, 7, and 10 of the '016 Patent.

1. Summary of the Asserted References

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

171. Senzaki is directed to a process for deposition of a multiple metal and metalloid compound layer with a compositional gradient of the metal and metalloid in the layer on a substrate of an electronic material. Ex. 1005 at Abstract. The process of Senzaki further includes varying the temperature of deposition from a first temperature to a second distinct temperature to result in the compositional gradient. *Id.* at Abstract; 2:33-57; 3:40-46; and 6:27-34.

172. Senzaki describes that in its “present invention” a new metal and metalloid deposition resulting in a compositional gradient is disclosed that can be used for precursor dispersing delivery methods, including direct liquid injection (DLI) in CVD applications. *Id.* at 3:3-6.

173. Senzaki states that it is “preferable” to vary the temperature during deposition in a constant manner from a low starting temperature to a high ending temperature. *Id.* at 4:25-28.

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

175. The varying deposition temperatures in the Senzaki examples resulted in varying deposition rates. *See Id.* (“the deposition rate increased from 450 to 560 angstroms per minute”; “the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute” and “deposition rate ranged from 285 to 320 angstroms per minute”).

176. The Petitioner incorrectly asserts, in its description of Senzaki, that Senzaki states that the film formed by CVD in example 1 could also be formed by ALD. ’664 Petition at 24. I disagree with this assertion. Senzaki does not state

that the precursors used in its example 1 can be used for both CVD and ALD, but rather asserts that certain precursors could be used with CVD “or” ALD without specifying which precursors would be suitable for use in an ALD process. Ex. 1005 at 4:4-9.

177. Finally, the Petitioner refers to Examples 1 and 2 of Senzaki, which employ the same precursor mixture to form both nitride and oxide films. As an initial matter, these examples include mixtures of two precursors, and not a single precursor. Further, given the unpredictability of precursor chemistry, it is not possible to generalize that any precursor can be used to form any desired film. Moreover, these examples of Senzaki are directed to CVD processes, and not ALD. As discussed above, it is not possible to predict with any reasonable degree of confidence which precursors may be appropriate to form desired film via an ALD process.

2. Petitioner’s Proposed Combination of Senzaki and Min Does Not Render Obvious Claims 1, 2, 7, and 10

178. In my opinion, a person of ordinary skill in the art would not have combined Senzaki and Min to arrive at the subject matter of Claims 1, 2, 7, or 10. In particular, a person of ordinary skill in the art would not have looked to combine the teachings of Senzaki with those of Min to arrive at a process for making an

insulator using a metal alkylamide to form a metal oxide by ALD, as required by Claims 1, 2, 7, and 10.

179. The Petitioner indicates that Senzaki does not disclose the subject matter of Claims 1, 2, 7, and 10. '664 Petition at 29. Specifically, Petitioner indicates that Senzaki does not disclose wherein deposition of the first reactant component and the second reactant component are self-limiting. *Id.* In my opinion, this is consistent with the understanding of a person of ordinary skill.

180. As the Petitioner recognizes, the deposition process recited by Claims 1, 2, 7, and 10 is a self-limiting ALD process with a specific type of precursor to form a specific type of insulator film. *Id.* Senzaki does not disclose any ALD process using a metal alkylamide to form a metal oxide layer.

181. I understand that Petitioner states that Senzaki's CVD examples can be modified in view of Min. '664 Petition at 33, 37-42. In particular the Petitioner argues that a person of ordinary skill "would have been motivated to ensure that Senzaki's deposition of reactants is self-limiting to achieve the benefits of ALD, including precise and accurate thickness control, film conformity, and 'single layer growth.' " '664 Petition at 33-34. For the reasons discussed below, I disagree.

a. A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Senzaki and Min to Arrive at the Process Recited by Claim 1 of the '016 Patent.

(1) A person of ordinary skill in the art would see that Senzaki and Min have directly contrary goals.

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

Specifically, the Petitioner argues that a person of ordinary skill in the art “would have been motivated to implement Min’s self-limiting teachings to achieve the goals of Senzaki and precisely control the thickness” of an insulator. *Id.* at 39. I disagree. In my opinion, the Petitioner ignores the express goals of Senzaki and Min which are completely contrary to each other.

183. First, a person of ordinary skill in the art would understand that Senzaki discloses the express goal of varying the temperature of deposition from a first temperature to a second distinct temperature to achieve a compositional gradient in the resulting film. Ex. 1005 at Abstract; 2:33-57; 3:40-46; and 6:27-34. Further, Senzaki states that it is “preferable” to vary the temperature during deposition in a constant manner from the low starting temperature to the high ending temperature. *Id.* at 4:25-28. Each of the examples in Senzaki purposely varies the deposition temperatures. See *Id.* at 5:10-6:21 (Examples 1-4) (“between 280 and 430°C”; “between 300 and 360°C”; “between 300 and 435°C”; and “between 310 and 350°C”).

184. Second, a person of ordinary skill in the art would recognize that the Senzaki goal of varying deposition temperatures of precursor mixtures results in varying deposition rates as shown in Senzaki's examples. See *Id.* ("the deposition rate increased from 450 to 560 angstroms per minute"; "the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute" and "deposition rate ranged from 285 to 320 angstroms per minute").

185. Third, as the Petitioner indicates, Min teaches as a goal self-limiting deposition as a distinct characteristic of an ALD process. '664 Petition at 38; see also Ex. 1006 at 9 (left). Further, Min teaches, and one of ordinary skill in the art would understand that in the desired goal of self-limiting deposition, "film thickness per cycle is independent of substrate temperature." Ex. 1006 at 8 (right).

186. It is common for ALD processes to exhibit an "ALD window" in temperature, where the growth rate of the process is constant due to the saturation and self-limiting behaviour of the chemical species at the surface. In fact, Fig. 3 on Min depicts such an ALD window in which the deposition rates is independent of deposition temperature. This is at odds with Senzaki. Modifying Senzaki based on Min to carry out the deposition used in an ALD window as shown in Min would not allow changing the deposition rate desired by Senzaki as the deposition rate would be independent of the deposition temperature within the ALD window. One would not expect a researcher normally skilled in the art of ALD to accept such

temperature variation as a proper practice. Thus, a person of ordinary skill in the art would not have been motivated to combine Senzaki with Min to obtain a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD because Senzaki and Min have directly conflicting goals regarding temperature control, deposition rates, and their associated effects on controlling the thickness of the film.

(2) A person of ordinary skill in the art would not have understood modifying Senzaki's CVD process in view of Min to yield predictable results nor be routine to implement.

187. The Petitioner argues that a person of ordinary skill would have understood that modifying Senzaki with Min would “yield predictable results and would have been routine to implement.” ‘664 Petition at 39. Particularly, the Petitioner points to Senzaki’s CVD example processes utilizing precursor mixtures containing a metal alkylamide and argues that one of ordinary skill in the art would be motivated to modify them based on Min’s teachings. *Id.* at 40, *see also* Ex. 1005 at 5:11-58 (examples 1 and 2). I disagree. In my opinion, Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min’s disclosure of ALD.

188. First, in my opinion, a person of ordinary skill in the art would not have modified the cited Senzaki CVD processes in view of Min due to the

unpredictable nature of ALD and CVD processes. One of ordinary skill would have known that a CVD process cannot be predictably adapted to ALD. *See* Ex. 2102 (concluding that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD precursors). *Min* itself found that films deposited by CVD were different than those deposited by ALD. *See* Ex. 1006 at 8 (identifying that TiN films deposited using TEMAT and NH₃ in an ALD process were different than those deposited in a CVD process). Additionally, as discussed above, a person of ordinary skill in the art would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD.

189. Further, the detailed description of *Senzaki* makes a single reference to ALD in a single paragraph consisting of eight lines of text, but fails to provide any specifics regarding how an ALD process would be implemented with the precursor mixtures or how ALD could be used to achieve a compositional gradient. Ex. 1005 at 4:8-15.

190. Second, a person of ordinary skill in the art would not have modified the cited *Senzaki* CVD processes in view of *Min* because *Min* discloses a highly specific ALD process and provides limited teachings. A person of ordinary skill in the art considering *Senzaki* in view of *Min* would have had no reasonable

expectation that the cited Senzaki CVD processes could be modified based on Min's specific ALD process.

191. A person of ordinary skill in the art would have recognized that Min is directed to the specific investigation of ALD using TEMAT and NH_3 to produce TiN films on SiO_2 . Ex. 1006 at Abstract. A person of ordinary skill in the art would have known that Min's specific teachings are not transferrable to all ALD processes. For example, Min identifies that its ALD process is not typical of other ALD processes because it deposited films with a thickness of 1.6ML/cycle. See Ex. 1006 at 10.

192. A person of ordinary skill in the art would recognize that Min provides no teachings with respect to the use of other reactants, such as oxygen or water, with metal alkylamides. Further, Min provides no teaching with respect to the deposition of films other than nitride films, such as oxides. In my opinion, a person of ordinary skill in the art would have no reasonable expectation based on Min's teachings that an ALD process using metal alkylamides with oxygen would successfully result in the deposition of a metal oxide film.

193. Thus, a person of ordinary skill in the art would not have expected that modifying the cited CVD deposition examples in Senzaki in view of Min would yield predictable results or would have been routine to implement as a

process for making a metal oxide film using an alkylamide precursor by self-limiting ALD.

(3) A person of ordinary skill in the art would not have known that certain precursors were “desirable” for ALD processes.

194. Petitioner argues that the precursors disclosed in Senzaki and Min “possess such characteristics as stability, volatility, and reactivity” and further that “[t]hese characteristics were known to be desirable in ALD precursors for self-limiting processes.” ‘664 Petition at 40. In my opinion, Petitioner’s argument ignores the state of the art at the time of Senzaki, Min and the ’016 Patent. A person of ordinary skill in the art would have understood that it was not possible to ascertain whether a precursor could be successfully used in an ALD process to form a metal oxide film without extensive experimentation. A person of ordinary skill in the art would have understood that volatility, thermal stability, and high reactivity are useful characteristics for precursors in both CVD and ALD. However, the fact that a precursor exhibited these characteristics would not provide a reasonable expectation that the precursor could have been successfully employed in a CVD or an ALD process. In fact, as discussed, there are precursors that are not suitable for use in CVD, but not ALD.

195. As stated before and as will be detailed further below, in this context it is inaccurate to state that metal alkylamides were known to be desirable for

forming metal oxide films via self-limiting ALD. This was not known at the time of the inventions. The Examiner correctly stated that the prior art, including the 1999 Min reference, taught the use of a metal alkylamide to form a titanium-silicon-nitride film by ALD, but did not teach or suggest forming a metal oxide by ALD using metal alkylamides. Ex.1002 at 24. I agree with the Examiner's reasons for allowance.

196. Although there is a vast amount of knowledge about general relationships in the chemical arts, chemistry is still largely empirical, and there is often great difficulty in predicting with a reasonable degree of confidence how a given compound will behave. See Ex. 2102.

(4) A person of ordinary skill in the art would have had no reasonable expectation of success modifying Senzaki's CVD process in view of Min.

197. The Petitioner argues that given Min's teaching, a person of ordinary skill in the art would have had a reasonable expectation of success in modifying the cited Senzaki CVD processes with Min's self-limiting ALD process. '664 Petition at 40-41. In particular, the Petitioner argues that "[o]ne of ordinary skill in the art would not have been deterred by the fact that Min describes formation of a metal nitride film rather than an insulator such as a metal oxide." Id. I disagree,

and in my opinion, the Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD.

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

199. For example, the data presented in Min's FIG. 3 shows a narrow temperature window, i.e., between 170°C and 210°C, in which the TiN film growth is self-limiting (a so-called ALD window). The ALD window depends not only on the properties of the precursor but also those of the reactant. Min indicates that TiN films "are not deposited below 150 C, indicating that reactant sources are mainly physisorbed on the surface below 150 C." Min explains that "[c]hemisorption involves the formation of relatively strong chemical bonds whereas in physisorption, the effective forces are of weak van der Waals type. Thus, weak bonds of physisorption can be easily purged by Ar." Ex. 1006 at 8. Min further explains that above 230 C, the deposition process transitions from an ALD process to an MOCVD process, which is not self-limiting. *Id.*

200. It is not, however, possible to predict with any reasonable degree of confidence whether changing any of the precursor or the reactant of an ALD system would result in a system for which an ALD window would be available.

For example, a change of the reactant may result in a system in which the chemisorption of the reactant would occur at such elevated temperatures at which the precursor would not be thermally stable. In fact, as discussed above, precursor-reactant systems are known that can be successfully used in a CVD process, but not in an ALD process because of the lack of a suitable ALD window (e.g., Tetramethysilane, $\text{Si}(\text{CH}_3)_4$).

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

202. Further, a person of ordinary skill in the art would have understood that modifying Min's ALD process to form an oxide film, rather than a nitride film that is the focus of Min's teachings, can pose a number of difficulties. A person of ordinary skill would understand that using a metal dialkylamide precursor to form a metal oxide involves the high possibility of the introduction of both carbon and nitrogen as impurities into the growing oxide film. See Ex. 2103; Ex. 2104; Ex. 2105; Ex. 2106. A person of ordinary skill would further recognize that the alternate introduction of a metal dialkylamide precursor and an oxidizing agent, as in ALD, onto a substrate would likely increase that possibility. The alternate introduction of a metal dialkylamide precursor and an oxidizing agent, onto a

substrate would likely result in the adsorption of at least part of the precursor on the substrate and its presence on the substrate surface by itself for a period of time prior to the introduction of the oxidizing agent. During such a period, carbon and nitrogen of the precursor could be incorporated into the growing film.

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

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

205. Thus, I believe that one of ordinary skill would not have looked to Min to adapt the cited CVD processes in Senzaki.

206. The Petitioner argues that the person of ordinary skill in art would not be deterred by the fact that Min only discloses the formation of nitride films

because “Senzaki teaches that the same precursor may be used to form either a metal oxide or a metal nitride film.” ‘664 Petition at 41. Again, I disagree. Each of the portions of Senzaki cited in support of this false premise are directed to CVD examples in which the temperature of deposition is being varied to result in a compositional gradient. *See* Ex. 1005 at 2:50-59, 4:22-44, and 5:11-58. These cited portions of Senzaki do not mention ALD and it is well known that the requirements of ALD precursors differ from those of CVD. Ex. 1012 at 13. Thus, any purported teaching by these sections of Senzaki must be limited to CVD.

207. Next, both the Petitioner and Dr. Banerjee incorrectly allege that “other prior art” references confirm that metal precursors may be used to form either a nitride or oxide film. Ex. 1003, at ¶ 134; ‘664 Petition at 41. The allegedly supporting references, however, are not directed to metal alkylamide precursors or only discuss CVD processes. *See* Ex. 1008 (providing no discussion of alkylamide precursors); Ex. 1011 (same); Ex. 1012 (same); Ex. 1013 (referring only to certain CVD processes).

208. As such, in my opinion, a person of ordinary skill would have no reasonable expectation of success in modifying the Senzaki CVD processes in view of Min to obtain a process for making a metal oxide film using an alkylamide precursor by self-limiting ALD.

(5) A person of ordinary skill in the art would not have found it obvious to try modifying Senzaki's CVD process in view of Min.

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

210. As discussed above, a person of ordinary skill in the art would understand that precursor chemistry is unpredictable and that one could not predict with any reasonable degree of confidence that the mixtures of precursors used in Senzaki could be successfully used in an ALD process to form an oxide film. More generally, a person of ordinary skill in the art would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work in an ALD process due to the different requirements of CVD and ALD.

211. Further, the Petitioner states that "such optimization of process conditions to achieve approximately one monolayer per ALD cycle is routine in semiconductor fabrication" and that Min teaches "advantages of monolayer deposition with self-limiting deposition conditions." '664 Petition at 42. However, as discussed above, one of ordinary skill in the art would have recognized that the goals of Senzaki are contrary to the alleged advantages of self-limiting deposition as taught in Min.

212. As stated above, a person of ordinary skill in the art would recognize that in Senzaki, varying deposition temperatures of precursor mixtures results in varying deposition rates as shown in Senzaki's examples. *See* Ex. 1005 at 5:10-6:21 ("the deposition rate increased from 450 to 560 angstroms per minute"; "the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute" and "deposition rate ranged from 285 to 320 angstroms per minute").

213. In Min, however, the growth rate of the deposited film is independent of the deposition temperature with the ALD window. Ex. 1006 at 8 (right) ("film thickness per cycle is independent of substrate temperature."). This advantage and characteristic of Min is directly at odds with the goals of Senzaki.

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

B. Grounds Based On Senzaki, Min, and Shin

215. It is my understanding that the Petitioner has alleged that Senzaki in view of Min and Shin renders obvious Claim 8 of the '016 Patent. '664 Petition at 4. Having reviewed, among other things, Senzaki, Min, Shin, the '664 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that

Senzaki in view of Min and Shin, as presented by the Petitioner, does not render obvious Claim 8 of the '016 Patent. Particularly, Senzaki in view of Min and Shin does not render obvious every element of independent Claim 1 as alleged in the Petition.

1. Petitioner's Proposed Combination of Senzaki, in view of Min, and Shin Do Not Render Obvious Claim 8

216. In my opinion, a person of ordinary skill in the art would not have combined Senzaki in view of Min and Shin to arrive at the subject matter of Claim 8. In particular, a person of ordinary skill in the art would not have looked to combine the teachings of Senzaki with those of Min and Shin to arrive at forming a metal oxide film using an alkylamide precursor, specifically tetrakis(ethylmethyamido)zirconium, in a self-limiting ALD process, as required by Claim 8.

217. Petitioner indicates that Senzaki and Min do not disclose the subject matter of Claim 8. '664 Petition at 45. Specifically, Petitioner indicates that Senzaki and Min do not disclose tetrakis(ethylmethyamido)zirconium. *Id.* As described above, a person of ordinary skill in the art would not be motivated to attempt to combine Senzaki and Min to achieve a process to form a metal oxide film using an alkylamide precursor in a self-limiting ALD process. In addition, a person of ordinary skill in the art would not have a reasonable expectation of

success in an attempt to combine Senzaki and Min to achieve a process to form a metal oxide film using an alkylamide precursor in a self-limiting ALD process. Shin does not provide this motivation or expectation of success, nor does the Petitioner assert that it does.

218. I understand that Petitioner indicates that one of ordinary skill would modify Senzaki's CVD process in view of Min and Shin. '664 Petition at 47. The Petitioner argues that a person of ordinary skill in the art "would have been motivated to perform Senzaki's ALD process in a self-limiting fashion as taught in Min, using tetrakis(ethylmethyldamino) zirconium as taught in Shin in order to use a metal dialkylamide precursor with characteristics comparable to the precursor disclosed in Senzaki, tetrakis(diethylamino) zirconium, but which may neutralize potential problems presented by tetrakis(diethylamino) zirconium as taught in Shin." '664 Petition at 47. For the reasons discussed below, I disagree.

a. A Person of Ordinary Skill in the Art Would not have been Motivated to Combine Senzaki, Min, and Shin to Arrive at the Process Recited by Claim 8 of the '016 Patent.

(1) A person of ordinary skill in the art would know that changes in alkyl groups of a precursor could cause non-linear unpredictable effects.

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

tetrakis(ethylmethyamino) zirconium (“Temaz”) only differs from a precursor disclosed in Senzaki by one alkyl group. ‘664 Petition at 48. I disagree.

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

221. It is my opinion that a person of ordinary skill in the art would know that there is a substantial degree of unpredictability in the pertinent area of chemical precursor design.

222. A person of ordinary skill in the art could not predict with any reasonable degree of confidence whether any given precursor compound or type would lead to successful atomic layer deposition.

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

223. The Petitioner argues that a person of ordinary skill would have been motivated to combine Senzaki in view of Min and Shin because Shin teaches that tetrakis(ethylmethylamino) zirconium may “neutralize” shortcomings of its diethylamino variant. ‘664 Petition at 49. I disagree.

224. In my opinion a person of ordinary skill would not be motivated to attempt the proposed combination because, for example, the person of ordinary skill in the art would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD.

225. As stated above, Shin is directed to CVD and makes no mention of ALD. Ex. 1007 at 6. There are significant differences between CVD and ALD processes, and hence precursors that may be suitable for a CVD process are not necessarily suitable for use in an ALD process. In fact, in 2006, a study concluded that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD. *See* Ex. 2102.

226. Thus, one of ordinary skill in the art would not be motivated to use tetrakis(ethylmethyldamino) zirconium in any ALD processes described in Senzaki and Min based on the CVD benefits taught in Shin.

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

227. The Petitioner argues that a person of ordinary skill in the art would have had a reasonable expectation of success in modifying Senzaki's process in view of Min's self-limiting ALD process using tetrakis(ethylmethyldamino) zirconium as taught in Shin. '664 Petition at 49. Particularly, the Petitioner argues that a person of ordinary skill would have had a reasonable expectation of success "because Min teaches that one of the precursors specifically described in Shin successfully achieves self-limiting ALD." *Id.* I disagree. In my opinion, the Petitioner ignores the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD.

228. First, in my opinion, a person of ordinary skill in the art would not have modified Senzaki's process, with Shin's CVD precursor in view of Min due to the unpredictable nature of ALD and CVD processes. One of ordinary skill would have known that there is no reasonable expectation that a CVD precursor can be successfully adapted to ALD. *See* Ex. 2102 (concluding that a large class of

compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD precursors). Min itself found that films deposited by CVD were different than those deposited by ALD. *See* Ex. 1006 at 8 (identifying that TiN films deposited using TEMAT and NH₃ in an ALD process were different than those deposited in a CVD process). Further, as noted by the Petitioner, Min is directed to tetrakis(ethylmethyldamino) titanium and Petitioner agrees that Min does not disclose tetrakis(ethylmethyldamido)zirconium as recited in Claim 8. *See* '664 Petition at 45 and Ex. 1006 at 7. Just because one CVD precursor described in Shin was found to be successful in achieving self-limiting ALD, it does not mean that the rest of the CVD precursors in Shin will work in ALD, nor does it mean that one of ordinary skill in the art would have a reasonable expectation of success for the use of Shin's CVD precursors in a self-limiting ALD process based on the reasons above.

(4) A person of ordinary skill in the art would not have found the proposed combination to be routine.

229. The Petitioner argues that "it would have been routine for one of ordinary skill to" modify Senzaki with Min in view of Shin to perform an ALD process in a self-limiting manner to form a metal oxide film using tetrakis(ethylmethyldamido)zirconium. '664 Petition at 50. Particularly, the Petitioner points to Min's teachings on the process of optimizing deposition

conditions so as to achieve self-limiting deposition as well as Shin's teaching that tetrakis(ethylmethyamido)zirconium "can be made easily". *Id.* at 50, *see also* Ex. 1007 at 7-9 (CVD precursor preparation). I disagree. In my opinion, Petitioner ignores the differences between CVD and ALD.

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

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

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

VIII. OPINIONS ON IPR2017-00666

A. Grounds Based on Vaartstra and Min

233. It is my understanding that the Petitioner has alleged that Vaartstra in view of Min renders obvious Claim 1 of the '016 Patent. '666 Petition at 4. Having reviewed, among other things, Vaartstra, Min, the '666 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Vaartstra in view of Min, as presented by the Petitioner, does not render obvious Claim 1 of the '016 Patent.

1. U.S. Patent No. 6,159,855, "Organometallic Compound Mixtures in Chemical Vapor Deposition" ("Vaartstra")

234. Vaartstra is directed to organometallic compound mixtures which include at least two metalloamide compounds, and to a CVD process for using the mixtures to form a multi-metallic layer on a substrate. Ex. 1006 at Abstract, 3:61-64.

235. Vaartstra discloses forming its compound mixtures for CVD by mixing two metalloamide compounds, for example, by mixing one or the other of

the metalloamide compounds with a solvent, and then adding the remaining metalloamide compound to the solvent/metalloamide mixture. *Id.* at 7:59- 8:17.

236. Vaartstra discloses that its compound mixtures can be used in a CVD process to form multi-metallic films, such as multi-metallic nitride, oxide, sulfide, boride, silicide, germanide, phosphide, arsenide, selenide, telluride, etc., on a substrate in a CVD chamber. *Id.* at Abstract, 10:41-45. “The precise chemical identity of the multi-metallic film will depend on the chemical identity of the metalloamide compounds, as well as the presence or absence of co-reactants.” *Id.* at 7:42-45. For example, “the presence of reactive gases, such as boranes, silanes, ammonia, hydrogen, etc., will impact on the chemical identity of the multi-metallic film.” *Id.* at 7:45-47.

237. Vaartstra discloses that CVD is a “particularly advantageous process because it allows for strict control of the thickness of the formed layer, and also because a wide variety of substrate geometries may be coated.” *Id.* at 1:49-52. Vaartstra identifies that CVD is used in semiconductor manufacturing and that for many applications, “obtaining and maintaining strict control over the stoichiometry of the deposited metallic or multi-metallic layer is paramount.” *Id.* at 1:57-60. Vaartstra discloses that “[t]he stoichiometry (i.e., numerical ratio of different metals and/or elements to one another) of the deposited layer can be strictly controlled if the precursors are delivered into the deposition chamber in a highly

uniform and regulated manner.” *Id.* at 1:64-2:1. However, Vaartstra identifies that the previously known methods of running a CVD process have not been able to effectively produce multi-metallic films having a stoichiometry within tight specifications. *See id.* at 2:39-42.

238. Vaartstra purports to solve the issues in the prior art by disclosing a process that is able to form multi-metallic films having metal stoichiometries within tight specifications. *See id.* at 2:38-45. In Vaartstra’s disclosed process, the compound mixtures can be vaporized, e.g., via a flash vaporization process, so as to form a multi-metallic vapor. *Id.* at 9:38-10:14. Through vaporization, the compound mixtures form a multi-metallic vapor having defined and controllable stoichiometry. *Id.* at Abstract. The multi-metallic vapor can then be transferred into a chemical vapor deposition chamber. *Id.* at 10:33-35. The metalloamide vapor can then be contacted with a substrate “under conditions of chemical vapor deposition” to a form a multi-metallic film on the substrate. *Id.* at Abstract, 10:41-45.

2. Petitioner’s Proposed Combination of Vaartstra and Min Does Not Render Obvious Claim 1

239. In my opinion, a person of ordinary skill in the art would not have combined Vaartstra and Min to arrive at the subject matter of Claim 1. In particular, a person of ordinary skill in the art would not have looked to combine

the teachings of Vaartstra with those of Min to arrive at a self-limiting ALD process using a metal alkylamide to form a metal oxide film, as required by Claim 1. *See* Ex. 1001 at 30:9-26 (Claim 1)

240. Petitioner indicates that Vaartstra does not disclose the subject matter of Claim 1. '666 Petition at 29-30. Specifically, Petitioner indicates that Vaartstra does not disclose a self-limiting ALD process using a metal alkylamide to produce a metal oxide film. *Id.* In my opinion, this is consistent with the understanding of a person of ordinary skill in the art.

241. As the Petitioner recognizes, the deposition process required by Claim 1 is a self-limiting ALD process. '666 Petition at 14. Claim 1 requires the use of a metal alkylamide in a self-limiting ALD process to produce a metal oxide film. *See* Ex. 1001 at 30:9-26 (Claim 1). Vaartstra does not disclose any such ALD process.

242. I understand that Petitioner indicates that one of ordinary skill would modify Vaartstra's CVD process in view of Min. '666 Petition at 29-30. The Petitioner argues that a person of ordinary skill in the art "would have been motivated to use Min's ALD technique with Vaartstra's metal dialkylamides and oxidants to form the claimed insulator in self-limiting fashion, thereby rendering Claim 1 obvious." '666 Petition at 30. For the reasons discussed below, I disagree.

a. A Person of Ordinary Skill in the Art Would Have Had No Expectation of Success Modifying Vaartstra's CVD Process in View of Min's ALD Process

243. The Petitioner argues that a person of ordinary skill in the art would have had a reasonable expectation of success in modifying Vaartstra's CVD Process in view of Min's ALD Process and would have expected predictable and beneficial results. '666 Petition at 43, 45. Particularly, the Petitioner argues that metal dialkylamides have characteristics that make them beneficial for ALD and "Min confirms that a species of Vaartstra's preferred metal dialkylamides may be successfully used in a self-limiting ALD process." *Id.* at 43-45. I disagree. In my opinion, the Petitioner over generalizes precursor chemistry and the differences between CVD and ALD, and mischaracterizes Min's disclosure of ALD.

244. First, in my opinion, a person of ordinary skill in the art would not have adapted Vaartstra's CVD process in view of Min due to the unpredictable nature of ALD and CVD processes. One of ordinary skill would have known that a CVD process cannot be predictably adapted to ALD. *See* Ex. 2102 (concluding that a large class of compounds developed to be particularly effective as CVD precursors fail to achieve growth that is needed for ALD precursors). Min itself found that films deposited by CVD were different than those deposited by ALD. *See* Ex. 1006 at 8 (identifying that TiN films deposited using TEMAT and NH₃ in an ALD process were different than those deposited in a CVD process).

245. A person of ordinary skill in the art would not have known that metal alkylamides are suitable as precursor for a self-limiting ALD process to produce a metal oxide film based on their characteristics, as alleged by the Petitioner. Petitioner alleges that a person of ordinary skill in the art would have looked to metal alkylamides because they are highly reactive, volatile, and thermally stable. *Id.* at 43-44. However, a person of ordinary skill in the art would know that these are useful characteristics for any deposition process and that they are shared by many compounds. However, the mere fact that a compound is reactive, volatile, and thermally stable, though useful, is not sufficient to predict with any reasonable degree of confidence that the compound can be used as a suitable precursor in an ALD process.

246. As the Petitioner recognizes, Vaartstra does not disclose an ALD process. *See id.* at 30. The only deposition process disclosed in Vaartstra is a CVD process. In a CVD process reactant vapors are selected that will allow for the continuous growth of a thin film on the heated surface. *See Ex. 1001* at 1:38-48. CVD processes are designed to allow a continuous thin film to form on the heated surface for as long as it is exposed to the reactant vapors.

247. In contrast, ALD, at least two reactant vapors are alternately exposed to a heated surface in the deposition chamber. Reactant vapors are specifically selected to allow for the controlled, stepwise growth of a thin film on a heated

surface. *See* Ex. 1015 at 13; *see also* Ex. 1001 at 20:56-21:8, 23:-60, 24:6-15, 24:28-38, 26:44-27:9, 27:45-30:7. A person of ordinary skill in the art would understand that ALD purposely avoids the continuous growth found in CVD by keeping the reactant vapors separate and by selecting reactant vapors with particular reactive characteristics that allow for controlled, stepwise growth.

248. As discussed above in Section VI.A.2.a(2), Petitioner's own cited references reveal difficulties in predicting whether a precursor would be suitable for use in an ALD process. *See, e.g.*, Ex. 1041, Goodman at 8 ("although the general conditions under which [ALD] would be possible seem reasonable [sic] clear, each material will have its own specific requirements regarding the operational conditions under which deposits of high perfection and purity could be obtained-while in some cases [ALD] might turn out not to be applicable.").

249. Additionally, as discussed above in Section VI.A.2.a(2), a person of ordinary skill in the art would know that precursors that are suitable for a CVD process cannot be necessarily assumed to work for an ALD process due to the different requirements of CVD and ALD

250. Second, a person of ordinary skill in the art would not have adapted Vaartstra's CVD process in view of Min because Min discloses a highly specific ALD process and its teachings are limited to the formation of TiN films. A person of ordinary skill in the art considering Vaartstra in view of Min would have had no

reasonable expectation that Vaartstra's CVD process could be successfully modified based on Min's specific ALD process so as to form a metal oxide film.

251. A person of ordinary skill in the art would have recognized that Min is directed to the specific investigation of ALD using TEMAT and NH_3 to produce TiN films on SiO_2 . Ex. 1006 at Abstract. A person of ordinary skill in the art would have known that Min's specific teachings are not transferrable to all ALD processes. For example, Min identifies that its ALD process is not typical of other ALD processes because it deposited films with a thickness of 1.6ML/cycle. See Ex. 1006 at 10 ("As shown in Fig. 7, saturated film thickness per cycle is 0.6 nm/cycle, which corresponds to 1.6 ML/cycle. However it has previously been reported that film thickness per cycle of the ALD process is limited to below 1 ML/cycle.").

252. Further, a person of ordinary skill in the art would have understood that Min's results are based on the specific reactants chosen for its ALD process, i.e., TEMAT and NH_3 . Min found that its ALD process using TEMAT and NH_3 was required to operate in the temperature range between 170°C and 210°C , based on its chosen reactants. *Id.* at 8. Min also found that the carbon contamination in the resulting film was also dependent on its chosen reactants. *Id.* at 10. Specifically, Min found that the use of NH_3 was required to reduce the carbon contamination in the deposited nitride film.

253. A person of ordinary skill in the art would recognize that Min provides no teachings with respect to other reactants, such as metal dialkylamides with water or alcohol. Further, Min provides no teaching with respect to the deposition of films other than nitride films, such as oxides. In view of Min, a person of ordinary skill in the art would have no reasonable expectation that an ALD process using metal dialkylamides with water or alcohol would successfully result in the deposition of a metal oxide film.

254. As such, in my opinion, a person of ordinary skill in the art would have no reasonable expectation of success in modifying Vaartstra's CVD process based on Min to produce an ALD process using metal dialkylamides and water or alcohol to produce a metal oxide film.

b. A Person of Ordinary Skill in the Art Would Not Have Been Motivated to Modify Vaartstra's Process in Light of Min

255. The Petitioner argues that a person of ordinary skill in the art would have been motivated to modify Vaartstra's CVD process to an ALD process such as that taught in Min "to achieve the benefits of ALD – one of which is a goal expressly taught in Vaartsrtra." '666 Petition at 39. In particular, Petitioner argues that a person of ordinary skill in the art would have adapted Vaartstra's CVD process to an ALD process to achieve the ability to deposit a stoichiometric film. *Id.* The Petitioner argues that "Vaartstra teaches that the ability to deposit a

stoichiometric film, which is a known benefit of ALD, is ‘paramount’ in many semiconductor applications.” *Id.* The Petitioner also argues that POSA would have been motivated to use the genus of metal dialkylamides taught in Vaartstra in an ALD process such as that taught in Min to form a metal oxide insulator because of the industry’s need for metal oxides formed using processes affording precise thickness control and other benefits of ALD.” I disagree with the Petitioner.

256. Vaartstra discloses that its process specifically achieves its goal of depositing a stoichiometric film and specifically identifies CVD as providing the desired thickness control. Ex. 1005 at 1:49-52; 2:39-42. A person of ordinary skill in the art would have had no motivation to modify Vaartstra’s process to achieve a goal that has already been achieved.

257. Vaartstra discloses a CVD process to effectively deposit multi-metallic films. Ex. 1005 at 2:39-42. Vaartstra highlights the benefits of CVD and identifies that CVD is used by the semiconductor industry in many production settings. *Id.* at 1:46-55. Vaartstra specifically identifies CVD as “a particularly advantageous process because it allows for strict control of the thickness of the formed layer, and also because a wide variety of substrate geometries may be coated.” *Id.* at 1:49-52. Vaartstra further identifies that in semiconductor manufacturing, strict control over the stoichiometry of a deposited multi-metallic layer is paramount. *Id.* at 1:57-60. Vaartstra states that the previously known

methods of running a CVD process have not been able to effectively produce multi-metallic films having a stoichiometry within tight specifications. *Id.* at 2:39-42. Vaartstra then discloses its process, which according to Vaartstra, solves the shortcomings of the prior art for depositing stoichiometric films. *Id.* at 2:44-45; *see also id.* generally.

258. In other words, Vaartstra provides a solution for controlling the stoichiometry of the deposited layer. Specifically, Vaartstra discloses that “[t]he stoichiometry (i.e., numerical ratio of different metals and/or elements to one another) of the deposited layer can be strictly controlled if the precursors are delivered into the deposition chamber in a highly uniform and regulated manner. In other words, it is highly desirable to control relative amounts of vaporized precursor molecules which are present in the deposition chamber of the MOCVD system. The delivery system is therefore an important component of the MOCVD process.” *Id.* at 1:64-2:6. Vaartstra explains that in conventional delivery systems, “bubblers are used in conjunction with a carrier gas stream which serves to dilute and deliver precursors into the deposition chamber.” *Id.* at 2:7-11. Vaartstra indicates that “[w]ith the use of conventional bubblers, however, the gas phase ratio of different precursors in the deposition chamber tends to vary, especially when the number of precursors (and hence bubblers) is increased. As a result, conventional bubblers are not very effective at providing strict control over the

composition of a vapor, and hence the composition of the deposited layer.” *Id.* at 2:11-18.

259. Vaartstra further indicates that flash vaporization has also been used to achieve a controlled delivery of a precursor into a deposition chamber. *Id.* at 2:19-21. Vaartstra, however, notes that “[a]lthough MOCVD and flash vaporization are known in the art, these processes have not, to date, been effectively used to produce multi-metallic films having metal stoichiometries within tight specification.” *Id.* at 2:38-42.

260. Vaartstra goes on to disclose a solution to this problem by providing a precursor that contains a mixture of two metalloamide compounds that “are particularly suitable for use in flash vaporization and chemical vapor deposition processes.” *Id.* at 2:48-49, 13:30-32. Further, Vaartstra teaches that “[t]he precise chemical composition of the deposited layer will depend not only on the composition of the source material, but also may be influenced by the presence of a reactant gas.” *Id.* at 10:58-61.

261. Nowhere does Vaartstra teach, or even suggest, that utilizing a process other than CVD would be needed to obtain a precise stoichiometry and thickness of a deposited film. Rather, Vaartstra directs one of ordinary skill in the art to the use of a mixture of metalloamide compounds, and delivering the mixture via a flash vaporization to obtain a multi-metallic film with a desired stoichiometry.

262. In my opinion, a person of ordinary skill in the art would have considered the teachings of Vaartstra as sufficient for forming oxide films and hence meet the industry's need for such films. I say this because Vaartstra represents that the use of its dialkylamide precursors in a CVD process achieves oxide films having desired properties. Further, modifying Vaartstra's teachings to deposit the multi-metallic film via an ALD process introduces additional complexity with regard to the delivery of a multi-metallic mixture and could lead to the contamination of the growing film with both carbon and nitrogen impurities.

263. The Petitioner also argues that "a POSA would have been motivated to combine the precursors and oxidants taught in Vaartstra with the ALD process taught in Min because of the similarities of the respective precursors and Vaartstra's teaching that the same precursors can be used to form both an oxide and a nitride." '666 Petition at 40. I disagree.

264. In my opinion, Min's teachings are limited to the use of ALD for forming TiN films and one of ordinary skill in the art would not have a reasonable expectation that those teachings could be successfully generalized to other systems, such as that proposed by the Petitioner.

265. For example, the data presented in Min's FIG. 3 shows a narrow temperature window, i.e., between 170°C to 210°C, in which the TiN film growth is self-limiting (a so-called "ALD window"). The ALD window depends not only

on the properties of the precursor but also those of the reactant. Min indicates that TiN films “are not deposited below 150°C, indicating that reactant sources are mainly physisorbed on the surface below 150°C.” Min explains that “[c]hemisorption involves the formation of relatively strong chemical bonds whereas in physisorption, the effective forces are of weak van der Waals type. Thus, weak bonds of physisorption can be easily purged by Ar.” Ex. 1006 at 8. Min further explains that above 230 C, the deposition process transitions from an ALD process to an MOCVD process, which is not self-limiting. *Id.*

266. It is not, however, possible to predict with any reasonable degree of confidence whether changing any of the precursor or the reactant of an ALD system would result in a system for which an ALD window would be available. For example, a change of the reactant may result in a system in which the chemisorption of the reactant would occur at such elevated temperatures at which the precursor would not be thermally stable. In fact, as discussed above, precursor-reactant systems are known that can be successfully used in a CVD process, but not in an ALD process because of the lack of a suitable ALD window (e.g., Tetramethysilane, $\text{Si}(\text{CH}_3)_4$).

267. In the present case, one of ordinary skill in the art would not have been able to predict with any reasonable degree of confidence whether replacing

ammonia with water in Min's system would result in a system for which an ALD window would be available.

268. Further, a person of ordinary skill in the art would have understood that modifying Min's ALD process to form an oxide film, rather than a nitride film which is the focus of Min's teachings, can pose a number of difficulties. For example, a person of ordinary skill would understand that using a metal dialkylamide precursor to form a metal oxide involves the high possibility of the introduction of both carbon and nitrogen as impurities into the growing oxide film. A person of ordinary skill in the art would further recognize that the alternate introduction of a metal dialkylamide precursor and an oxidizing agent, as in ALD, onto a substrate would likely increase that possibility. The alternate introduction of a metal dialkylamide precursor and an oxidizing agent, onto a substrate would likely result in the adsorption of at least part of the precursor on the substrate and its presence on the substrate surface by itself for a period of time prior to the introduction of the oxidizing agent. During such a period, carbon and nitrogen of the precursor could be incorporated into the growing film.

269. In Min, nitrogen is a constituent of the TiN film. As such, in Min, the nitrogen of the dialkylamide precursor is not a potential undesired impurity. In other words, in Min, only the carbon of the dialkylamide precursor would be a potential impurity in the growing film. In contrast, if one were to use a

dialkylamide precursor to form an oxide film, both nitrogen and oxygen of the precursor would be potential impurities.

270. A person of ordinary skill in the art would have understood that as taught in Vaartstra, Min's use of ammonia as a reactant reduces carbon impurities. Ex. 1006 at 11:4-7 ("The use of ammonia may be particularly useful to prepare a film with less carbon content than is typically obtained using only an inert atmosphere (e.g., argon) as a carrier gas."). Ammonia, however, cannot be used a reactant to provide the oxygen source necessary to form a metal oxide film. As such, one of ordinary skill would understand that the teachings of Min regarding the formation of a TiN film is not simply transferrable to the formation of a metal oxide film.

271. Thus, I believe that one of ordinary skill in the art would not have looked to Min to modify the CVD process in Vaartstra.

B. Grounds Based on Vaartstra, Min, and Ma

272. It is my understanding that the Petitioner has alleged that Vaartstra in view of Min and Ma renders obvious Claims 2-3, 6-7, and 9-10 of the '016 Patent. '666 Petition at 4. Having reviewed, among other things, Vaartstra, Min, Ma, the '666 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Vaartstra in view of Min and Ma, as presented by the Petitioner, does not render obvious Claims 2-3, 6-7, and 9-10 of the '016 Patent.

1. U.S. Patent No. 6,200,866, “Use of silicon germanium and other alloys as the replacement gate for the fabrication of MOSFET” (“Ma”)

273. Ma is directed to a method for the manufacture of integrated circuits, and specifically for the manufacture of MOSFET devices formed using a replacement gate. Ex. 1007 at Abstract; 1:12-14. Ma’s method involves the steps of:

depositing an oxide layer on a silicon substrate for device isolation; forming a silicon based alloy island above a gate region in the substrate, wherein the silicon based alloy comprises a silicon germanium alloy or a silicon tin alloy or another alloy of Group IV-B elements; building a sidewall about the silicon based alloy island; forming a source region and a drain region in the substrate; removing the silicon based alloy island, thereby leaving a void over the gate region; filling the void and the areas over the source region and the drain region; and planarizing the upper surface of the structure by chemical mechanical polishing.

Id. at Abstract.

2. Vaartstra, Min, and Ma Do Not Render Obvious Claims 2, 3, 6, 7, 9, and 10

274. For the same reasons discuss above, the combination of Vaartstra, Min and Ma do no render obvious Claims 2, 3, 6, 7, 9, and 10.

C. Grounds Based on Vaartstra, Min, Ma, and Bradley II

275. It is my understanding that the Petitioner has alleged that Vaartstra in view of Min, Ma, and Bradley II renders obvious Claim 5 of the ’016 Patent. ’666

Petition at 5. Having reviewed, among other things, Vaartstra, Min, Ma, Bradley II the '663 Banerjee Declaration, and Petitioner's support for its allegations, it is my opinion that Vaartstra in view of Min, Ma, and Bradley II, as presented by the Petitioner, does not render obvious Claim 5 of the '016 Patent.

1. D.C. Bradley et al., “Metallo-organic Compounds Containing Metal-Nitrogen Bonds. Part VI. Infrared and Nuclear Magnetic Resonance of Dialkylamido-derivatives of Titanium, Vanadium, Zirconium, Niobium, Hafnium, Tantalum, and Thorium” (“Bradley II”)

276. Bradley II is directed to the infrared and nuclear magnetic resonance of dialkylamido-derivatives of titanium, vanadium, zirconium, niobium, hafnium, tantalum, and thorium. Ex. 1008 at Abstract. Bradley II discusses the experimental setup with respect to its infrared and nuclear magnetic resonance techniques and provides and discusses the results obtained. *See generally id.* Bradley II focuses on the assignment of characteristic bands and discusses the metal-nitrogen stretching frequencies in terms of a significant contribution of nitrogen to metal bonding. *Id.* at Abstract.

2. A Person of Ordinary Skill in the Art Would have no Motivation to Combine the Teachings of Bradley II with Vaartstra, Min, and Ma

277. The Petitioner argues that a person of ordinary skill in the art would have been motivated to combine the teachings of Vaartstra, Min, and Ma with Bradley II to use tetrakis(dimethylamido) hafnium as the dialkylamide precursor in

a self-limiting ALD process to form a metal oxide film. See '666 Petition at 57-60. Particularly, the Petitioner argues that a person of ordinary skill in the art would have been motivated “to use Vaartstra’s genus of preferred metal dialkylamide in a self-limiting ALD process as taught in Min to form a gate insulator as taught in Ma, using tetrakis(dimethylamido) hafnium, as taught in Bradley II, as a metal alkylamide precursor, in order to avoid steric hindrance and use a precursor that has a low number of carbon atoms.” *Id.* at 58-59. I disagree.

278. In my opinion, a person of ordinary skill in the art would have no motivation to combine the teachings of Bradley II with Vaartstra, Min, and Ma. As stated above, Bradley is directed to the infrared and nuclear magnetic resonance of dialkylamido-derivatives of titanium, vanadium, zirconium, niobium, hafnium, tantalum, and thorium. Ex. 1008 at Abstract. Bradley II provides no discussion regarding whether the compounds considered its experiments would be suitable for a CVD or ALD process. In fact, Bradley II makes no mention of any deposition process.

279. The Petitioner argues that Vaartstra provides express motivation to combine its teachings with Bradley II because Vaartstra “stat[es] that it is ‘typically desirable’ that a metalloamide compound for use as a precursor have ‘no more than about 20 carbon atoms, preferably has from 1 to about 10 carbon atoms, and more preferably has 1 to about 5 carbon atoms.’” ’666 Petition at 59.

However, such a disclosure would not have led a person of ordinary skill in the art to look to Bradley II to find tetrakis(dimethylamido) hafnium and to use it as a precursor in a self-limiting ALD process to form a metal oxide film.

280. First, as discussed above, Vaartstra is solely directed to the use of compounds in CVD processes. A person of ordinary skill in the art would not have understood Vaartstra's disclosure to apply to ALD process. Second, such a disclosure provides no guidance for a person of ordinary skill in the art to look past the compounds disclosed in Vaartstra for additional compounds. Certainly, it does not direct a person of ordinary skill in the art to look to the teachings of Bradley II, which is directed to the infrared and nuclear magnetic resonance of certain dialkylamido-derivatives. Third, for all the reasons discussed above, a person of ordinary skill in the art would not know with any reasonable degree of confidence whether tetrakis(dimethylamido) hafnium could be successfully used in a self-limiting ALD process to produce a metal oxide film.

D. Grounds Based on Vaartstra, Min, Ma, and Shin

281. It is my understanding that the Petitioner has alleged that Vaartstra in view of Min, Ma, and Shin renders obvious Claim 8 of the '016 Patent. '666 Petition at 5. Having reviewed, among other things, Vaartstra, Min, Ma, Shin the '666 Banerjee Declaration, and Petitioner's support for its allegations, it is my

opinion that Vaartstra in view of Min, Ma, and Shin, as presented by the Petitioner, does not render obvious Claim 8 of the '016 Patent.

1. Vaartstra, Min, Ma, and Shin Do Not Render Obvious Claim 8

282. For the same reasons discuss above, the combination of Vaartstra, Min, Ma and Shin do no render obvious Claims 8.

283. I declare under the penalty of perjury that all statements made in this Declaration are true and correct.

Dated: 4/30/2017

By: 
Wayne L. Gladfelter, Ph.D.

EXHIBIT A

Curriculum Vitae

Wayne L. Gladfelter

(as of August 16, 2016)

EDUCATION

Ph.D., Inorganic and Organic Chemistry, The Pennsylvania State University (1978)
B.S., Mineral Engineering Chemistry, Colorado School of Mines (1975)

PROFESSIONAL EXPERIENCE

Associate Dean of Academic Affairs (2008-2013)
Interim Associate Dean of Academic Affairs (2007-2008)
Professor of Chemistry, University of Minnesota (1988-present)
Department of Chemistry Chair (1999 - 2005)
Associate Director of the Materials Characterization Facility (1996 - 1999)
Member of Graduate Faculty, Chemical Engineering (1994 - present)
Member of Graduate Faculty, Materials Science and Engineering (1991-present)
Associate Professor of Chemistry, University of Minnesota (1984-1988)
Director of Graduate Studies, University of Minnesota (1984-1986)
Assistant Professor of Chemistry, University of Minnesota (1979-1984)
NSF Postdoctoral Fellow, California Institute of Technology (1978-1979)

HONORS AND AWARDS

College of Science and Engineering Taylor Award for Service (2015)
Fellow of the AAAS (2007)
Associate Fellow of the Minnesota Supercomputing Institute (2005)
Colorado School of Mines "Wall of Fame" Award (2003)
Institute of Technology Distinguished Professorship (1998)
Institute of Technology Student Board Outstanding Instructor Award (1991)
Alfred P. Sloan Research Fellow (1983-1985)
Union Carbide Innovation Recognition Program (1982-1985)
Nobel Laureate Signature Award for a Graduate Student in Chemistry, American Chemical Society (ACS) (1980)
National Science Foundation National Needs Post-Doctoral Fellowship, California Institute of Technology (1978-1979)
Sigma Xi Research Award, The Pennsylvania State University (1978)
Central Pennsylvania American Chemical Society Graduate Student Award, The Pennsylvania State University (1978)
Harry Bright Scholarship, The Pennsylvania State University (1977)

R.A. Baxter Award in Chemistry, Colorado School of Mines (1975)

SELECTED PROFESSIONAL SERVICE

Editorial Advisory Board of *Journal of Coordination Chemistry* (2010-present)
Editorial Advisory Board of *Inorganic Chemistry* (2013-2016)
Co-Chair of MRS Symposium on Photovoltaics and Optoelectronics from Nanoparticles (Spring Meeting, 2010)
Chair Elect, Chair and Past Chair of Chemistry Section of AAAS (2007 - 2009)
Co-Chair of ACS Symposium on CVD and ALD (Fall Meeting, 2007)
Committee of Visitors, NSF Division of Chemistry Review Board (2004)
International Editorial Board of *Ceramics International* (2002 - 2007)
Executive Committee Member of the ACS Division of Inorganic Chemistry (2002 -2004)
General Chair of the 34th Great Lakes Regional ACS Meeting (2002)
Executive Committee of the Council for Chemical Research (2003 - 2004)
Governing Board of the Council for Chemical Research (2002 - 2004)
Co-chair of the Gordon Research Conference on Chemistry of Electronic Materials (2001)
Editorial Advisory Board of *Chemical Vapor Deposition* (1994 - present)
Section Editor of *CHEMTRACTS - Inorganic Chemistry* (1997 - 2001)
Treasurer of the ACS Division of Inorganic Chemistry (1993 - 1997)
Editorial Advisory Board of *Chemistry of Materials* (1990 - 1996 and 2003 - 2008)

STUDENT AND POSTDOCTORAL ASSOCIATE ADVISING

- Graduated 43 PhDs in Chemistry
- Graduated 3 PhDs in Materials Science
- Graduated 2 PhDs in Chemical Engineering
- Graduated 6 MSs in Chemistry
- Mentored 15 postdoctoral associates
- Advised 65 undergraduate researchers

SUMMARY OF PUBLICATION AND PRESENTATION ACTIVITY

- 189 refereed articles in primary journals
- 52 refereed contributions to edited volumes and conference proceedings
- 10 refereed review articles
- 7 patents