

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

MICRON TECHNOLOGY, INC.,
Petitioner,

v.

PRESIDENT AND FELLOWS OF HARVARD COLLEGE,
Patent Owner

Case IPR Nos.: 2017-00662
2017-00663
2017-00664

U.S. Patent Nos. 6,969,539 and 8,334,016
Title: VAPOR DEPOSITION OF METAL OXIDES, SILICATES, AND
PHOSPHATES, AND SILICON DIOXIDE

**Declaration of Sanjay Banerjee, Ph.D. in Support of Reply to Patent Owner’s
Responses**

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P.O. Box 1450
Alexandria, VA 22313-1450

I, Sanjay Banerjee, hereby declare as follows:

I. INTRODUCTION

1. I understand that the following grounds from IPR2017-00662, IPR2017-00663, and IPR2017-00664 have been instituted and are at issue in these proceedings:

Proceeding	Grounds
IPR2017-00662	1. Anticipation of claims 24, 26, and 29 of the 539 Patent by Buchanan 2. Obviousness of claims 24, 26, and 29 of the 539 Patent over Buchanan combined with the knowledge of a POSA
IPR2017-00663	1. Obviousness of claims 1-3, 5-7, 9, and 10 of the 016 Patent over Buchanan combined with Min 2. Obviousness of claim 8 of the 016 Patent over Buchanan combined with Min and Shin
IPR2017-00664	1. Obviousness of claims 1, 2, 7, and 10 of the 016 Patent over Senzaki combined with Min 2. Obviousness of claim 8 of the 016 Patent over Senzaki combined with Min and Shin

2. I note that the exhibits used in these proceedings do not all share the same exhibit numbers. For ease of reference, my discussion below will use the short-form exhibit name as set forth in the parties' respective exhibit lists, where possible (*e.g.*, "Buchanan" refers to U.S. Patent No. 6,984,591, etc.). Where no short-form name has been given, or where multiple exhibits have the same or confusingly similar short-form names, I will cite the exhibit by its exhibit number, identifying by case number the proceeding to which that exhibit number corresponds (*e.g.*, "Ex.1032 (IPR2017-00662)" would refer to Exhibit 1032 submitted in the 662 proceeding).

II. MATERIALS RELIED ON IN FORMING MY OPINIONS

3. In addition to the materials identified in my initial declarations in these proceedings (Ex.1003 in each respective proceeding), I have reviewed and considered Harvard's Patent Owner Preliminary Responses in each proceeding, Harvard's Patent Owner Responses in each proceeding, the declarations submitted by Harvard's expert, Dr. Wayne Gladfelter, in each proceeding, and the materials cited therein. I have also reviewed and considered Dr. Gladfelter's deposition testimony in these proceedings and the exhibits to his deposition. I have further reviewed and considered the materials and exhibits cited herein.

III. OPINIONS REGARDING THE STATE OF THE ART AND KNOWLEDGE OF A POSA

4. While I provided an overview of the state of the relevant art in my initial declarations that were submitted with the Petitions, PO and Dr. Gladfelter raised certain new arguments and issues in the Patent Owner Responses and accompanying declarations to which I respond here.

A. Predictability Of ALD Chemistry

5. I understand that PO and Dr. Gladfelter have asserted that a POSA would not have been able to reasonably predict whether metal dialkylamide precursors disclosed in the prior art could be used to deposit metal oxide films in ALD processes without actually performing an experiment. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 6; Patent Owner Response (IPR2017-00663), at p. 4; Patent Owner Response (IPR2017-00664), at pp. 6-7. I disagree. As I explained in my deposition, a POSA considering a metal dialkylamide precursor would have determined, with reasonable predictability, from the basic physical, chemical, and thermodynamic properties of metal dialkylamides whether or not they could be successfully employed as ALD precursors. These properties include bond strengths, vapor pressures, melting points, and evaporation points, and could be readily looked up in standard chemical handbooks and references. One such reference is the CRC Handbook of Chemistry and Physics, which was

commonly used and relied upon by those of ordinary skill in this field of art in the 1999-2000 timeframe and through the present day.

6. Additionally, a POSA would have determined with reasonable predictability that a particular precursor would be effective in ALD by looking to binary CVD reactions (*i.e.*, CVD reactions that deposit a film by reacting two different precursors together) that correspond to the half-reactions of the proposed ALD process. For example, to determine whether tetrakis(diethylamino) zirconium and oxygen would be suitable precursors for an ALD reaction to deposit zirconium oxide, a POSA could look to a CVD process using these two same precursors. This general correlation was described in the prior art, of which a POSA would have been aware in the relevant time period. George, for example, described that "the ALE approach is most appropriate for binary compounds because a *binary chemical vapor deposition reaction* can easily be separated into two half-reactions." George, p. 5. Similarly, Leskelä II observed that while ALD had unique features that differentiated it from CVD, "the unique features of ALD are not that much reflected in the choices of single precursor molecules *which are essentially the same as those used in CVD.*" Leskelä II, p. 15. Even as ALD continued to develop and the technique was optimized for additional precursors, this correlation continued to hold. A 2001 article, for example, observed that "[g]enerally speaking, precursors similar to those used in CVD are also applicable

to an ALE process provided that certain requirements, such as thermal stability and sufficiently high reactivity, are met." Putkonen (Ex.1068 (IPR2017-00662); Ex.1066 (IPR2017-00663); Ex.1064 (IPR2017-00664)), p. 1. As I noted in my opening declarations, metal dialkylamides were known to have the volatility, thermal stability, and high reactivity for ALD. While this general correlation between binary CVD precursors and ALD precursors is not absolute, in my opinion it would have provided a POSA with more than a reasonable expectation of success in taking a proven binary CVD precursor pairing and using the two precursors in an ALD process. Thus, for example, the fact that Bastianini disclosed the successful use of tetrakis(diethylamino)zirconium and oxygen to deposit zirconium oxide in a CVD reaction would have allowed a POSA to predict, with reasonable certainty, that tetrakis(diethylamino)zirconium and oxygen also could be used in an ALD reaction to deposit zirconium oxide. See Bastianini, p. 17.

7. Dr. Gladfelter is of the opinion that CVD precursors could not be used to predict ALD precursors, but it appears that Dr. Gladfelter's opinions are phrased so that they refer to both binary CVD and single source CVD. See, e.g., Patent Owner Response (IPR2017-00662), at pp. 7-8; see also *id.* at pp. 25-26 (citing Gross and Dorman, which discuss CVD deposition by pyrolysis of $\text{Co}_2(\text{CO})_8$, i.e., single-source CVD using $\text{Co}_2(\text{CO})_8$); Patent Owner Response (IPR2017-00663), at

pp. 4-5, 19-20; Patent Owner Response (IPR2017-00664), at pp. 7-8. Single source CVD is not comparable to binary CVD or ALD, because single source CVD deposits films by decomposing a *single* precursor compound. Because ALD reactions always involve two or more different precursors that are exposed to the substrate sequentially, a POSA would not have looked to single source CVD art to determine whether precursors would work for ALD. Colombo, for example describes single source CVD of metal oxide films in which the precursors "cleave directly to metal oxide films." Colombo, p. 5. In ALD of metal oxide films, by contrast, surface-bound hydroxyl groups often play an important role as reaction intermediates, signaling that the reaction mechanism in ALD differs significantly from the "directly cleaving" mechanism of single source CVD. *See, e.g.,* Juppo, pp. 2-3.

8. A POSA also would have been able to predict with reasonable certainty that metal dialkylamides with metal atoms from a particular column of the periodic table would be effective as ALD precursors if a metal dialkylamide of another metal from the same column had already been successfully used in ALD, because for purposes of vapor deposition processes, dialkylamides of metals in the same column of the periodic table generally share common characteristics. Dr. Gladfelter confirmed this in his deposition, testifying that he "would agree that it enhances the predictability" when one considers alkylamides of metals that are in a

particular column of the periodic table. Gladfelter Dep., at 209:10-23. Thus, for example, the fact that Min and Leskelä 865 both disclose using titanium dialkylamides in ALD reactions to deposit titanium nitrides and titanium-containing oxides, respectively, would have allowed a POSA to predict, with reasonable certainty, that dialkylamides of other Group IVB metals such as zirconium and hafnium could likewise be used in ALD reactions. See Min, p. 7; Leskelä 865, 7:6-23.

9. Additionally, I note that the fact that a POSA would have performed an experiment as part of the process of verifying the effectiveness of ALD precursors does not mean that the experiment was needed in order to provide a reasonable expectation of success. In fact, it is commonplace in the study of vapor deposition reactions for those of skill in the art to confirm their hypotheses by running experiments even when they already have a very high expectation that their hypotheses are correct; it is simply part and parcel of the scientific method. Conversely, a POSA also would not abandon an investigation simply because he lacked absolute, 100% certainty of the outcome prior to running an experiment. A POSA would have understood that confirming experimentation is a routine and integral part of the practice of vapor deposition reactions.

**B. Optimization Of ALD Process Conditions For New Precursors
Was Straightforward And Routine**

10. PO and Dr. Gladfelter argue that a POSA would not have been able to adapt ALD processes for the use of new precursors without "extensive" experimentation. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 6; Patent Owner Response (IPR2017-00663), at p. 4; Patent Owner Response (IPR2017-00664), at pp. 6-7. I disagree. As I stated in my opening declarations, adjusting deposition conditions for an ALD process is a routine optimization process that is well within the abilities of a POSA, and it is routinely done by researchers to study film deposition characteristics across temperature ranges (*e.g.*, to identify the ALD window for a particular reaction). *See, e.g.*, Min, pp. 8-9. As shown in Min, the process is not difficult, and simply involves running the reaction at different substrate temperatures and measuring the growth rate at each temperature. *Id.* As I explained in my deposition, a researcher literally "dials in" the desired temperature using a dial, knob, or other equivalent control that is built into the ALD equipment. Banerjee Tr., 28:20-29:2. This procedure is also not particularly time consuming; as I indicated in my opening declaration, it is typical for facilities engaging in ALD research to have multiple ALD reactors available for testing and process optimization, which allows the researchers to test multiple different process conditions and/or multiple different precursors in parallel. My laboratory at UT, for example, has 3 ALD reactors available for simultaneous use.

C. Metal Alkylamides Were Known To Be Suitable For ALD

11. As I noted in my opening declarations, to be suitable for ALD, a precursor should be highly reactive, volatile, and thermally stable against decomposition. *See, e.g.*, Ex.1003 (IPR2017-00662), ¶57; Ex.1003 (IPR2017-00663), ¶57; Ex.1003 (IPR2017-00664), ¶57. Metal dialkylamides were known to possess these properties, and therefore a POSA would have understood them to be suitable precursor compounds for ALD. *See, e.g.*, Ex.1003 (IPR2017-00662), ¶¶62-63; Ex.1003 (IPR2017-00663), ¶¶62-63; Ex.1003 (IPR2017-00664), ¶¶62-63; Bradley II, p. 5; Tsyganova, p. 6; Vaartstra, 4:65-5:12, 5:54-57; Ex.1034 (IPR2017-00662), at pp. 6-7. I understand that PO and Dr. Gladfelter dispute whether possessing these properties is sufficient to make a precursor suitable for ALD (*see, e.g.*, Patent Owner Response (IPR2017-00662), at p. 61), but I note that PO cited a paper to the Patent Office during prosecution of the 016 Patent that applied these same criteria to determine the suitability of ALD precursors. In particular, the Jones paper submitted as an exhibit in these proceedings by Harvard lists volatility, thermal stability, and reactivity as indicating "the appropriate physical properties and *suitable* deposition chemistry" of ALD precursors. Jones, p. 2. Based on my review of Jones, the authors do not identify any additional criteria as being necessary for a substance to be a "suitable" ALD precursor. I also note that PO cited the Jones reference to the USPTO during prosecution of the 016 Patent. A POSA reviewing the file history of the 016 Patent and the Jones paper

therefore would have concluded that Harvard, in representing to the USPTO that the Jones article was indicative of the state of the art, was in agreement with Jones that these properties—and not the additional properties cited by Dr. Gladfelter (*see, e.g.,* Ex.2116 (IPR2017-00662), ¶44; Ex.2116 (IPR2017-00663), ¶46; Ex.2120 (IPR2017-00664), ¶46)—determine whether a substance is suitable as an ALD precursor. While Dr. Gladfelter cites Leskelä II for the additional properties he lists in his declarations, a POSA would not understand Leskelä II to teach that *all* of these properties are required for a *suitable* ALD precursor. For example, Leskelä II states that reaction side-products “should” not further react or adsorb to the surface, “should” not react with the film and cause etching, and “should” not dissolve in the film. Leskelä II, p. 14. A POSA would have understood that these properties affect film *quality*, rather than precursor *suitability*. For example, although Leskelä II states that reaction side-products should not react or adsorb on the surface, it nonetheless notes that the reaction between metal chlorides, “often used in the ALD growth of oxide films,” produces hydrochloric acid, which can readsorb or react. *Id.* A POSA would not have understood this to mean that metal chlorides are not suitable ALD precursors, because Leskelä II clearly indicates that they are suitable, being “often used in the ALD growth of oxide films.” *Id.* Rather, a POSA would have understood that the tendency of hydrochloric acid to react with the surface is one factor that must be considered in cases where film

quality (*e.g.*, uniformity, conformality, step coverage, etc.) is important to the intended application.

12. Additionally, I note that the challenged claims of both the 539 and 016 Patents do not include any requirements as to the quality of the deposited metal oxide or oxygen-containing insulator film. In other words, the claims do not require the films to meet any particular criteria in terms of defects, contamination or impurity levels, conformality, step coverage, or the like. Thus, a POSA's expectation of being able to successfully perform the claimed processes, which just require depositing a metal oxide or oxygen-containing insulator film, would not have been impacted by considerations of whether using a metal dialkylamide precursor would have yielded films of a particular quality.

D. Use Of Metal Dialkylamides In Metal Oxide ALD

13. PO and Dr. Gladfelter dispute that before 2000, the prior art had described and/or taught ALD to form metal oxides using metal dialkylamide precursors. *See, e.g.*, Ex.2116 (IPR2017-00662), ¶24; Ex.2116 (IPR2017-00663), ¶23; Ex.2120 (IPR2017-00664), ¶23. PO and Dr. Gladfelter are clearly incorrect. In addition to the disclosures and teachings of Buchanan and Senzaki, which I discussed in my opening declarations, a POSA would have been aware of, for example, PCT Publication No. WO 00/15865 ("Leskelä 865"), which published on March 23, 2000 and was filed with the World Intellectual Property Organization on

September 13, 1999. In its disclosure, it describes ALD processes that use "a volatile titanium compound," including "alkylamino complexes of titanium" such as tetrakis(diethylamino) titanium, tetrakis(dimethylamino) titanium, tetrakis(ethylmethylamino) titanium, and tetrakis(isopropylmethylamino) titanium, in conjunction with barium and/or strontium precursors and a reactive oxygen precursor such as water or hydrogen peroxide to deposit barium-titanium, strontium-titanium, and barium-strontium-titanium oxide films. Leskelä 865, 7:6-23. Thus, it is clear that the prior art had taught using metal dialkylamides to form metal oxide films through ALD processes before 2000.

E. Contamination From Metal Alkylamides

14. Harvard and Dr. Gladfelter assert that the prior art shows that metal dialkylamides, when used to deposit films in CVD, caused significant carbon and nitrogen contamination of the resulting films. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 63; Patent Owner Response (IPR2017-00663), at p. 50; Patent Owner Response (IPR2017-00664), at 9. Harvard and Dr. Gladfelter further argue that this would have deterred a POSA from considering metal dialkylamides as a precursor in ALD reactions. Patent Owner Response (IPR2017-00662), at p. 63; Patent Owner Response (IPR2017-00663), at p. 50; Patent Owner Response (IPR2017-00664), at 9. I disagree for several reasons.

15. First, many of the CVD papers that Dr. Gladfelter cites are single-source CVD studies. *See, e.g.*, Ex.2116 (IPR2017-00662), ¶27 (citing papers); Ex.2116 (IPR2017-00663), ¶28; Ex.2120 (IPR2017-00664), ¶27; Patent Owner Response (IPR2017-00662), at p. 64; Patent Owner Response (IPR2017-00663), at p. 51; Patent Owner Response (IPR2017-00664), at 9. As I discussed above, a POSA would have known that single source CVD is not comparable to ALD, because the former involves only a single precursor. A POSA therefore would not have based his evaluation of a potential ALD precursor on single source CVD experiments using that same precursor. The Fix, Sugiyama, Ishihara, and Katz papers cited by Harvard and Dr. Gladfelter all describe single-source CVD reactions.

16. Additionally, the Dubois 92 and Dubois 94 papers cited by Dr. Gladfelter actually contradict Dr. Gladfelter's conclusions. The Dubois papers examined both single source CVD of tetrakis(ethylmethlamino) titanium ("TEMAT") and binary CVD of TEMAT with ammonia, finding that when TEMAT is thermally decomposed without a second reactant (*i.e.*, single source CVD), it formed titanium-nitrogen-carbon metallocycle intermediates in the gas phase that led to carbon impurities in the ultimate titanium nitride film. Dubois 92, pp. 6-7; Dubois 94, pp. 2-3. When a second reactant was introduced, converting the reaction into a binary CVD reaction, formation of the metallocycle

intermediate was avoided, resulting in decreased carbon contamination. Dubois 92, pp. 6-7; Dubois 94, pp. 1, 2-4. Because ALD *always* involves at least two different precursors, a POSA would have expected from these articles that ALD films deposited using metal dialkylamide precursors would not have significant impurities, because these articles teach that the presence of a second reactant reduces the occurrence of impurities to negligible levels. This is also consistent with other prior art of which a POSA would have been aware. A different Fix article, for example, which was co-authored by Dr. Gordon, the lead inventor of the 539 and 016 Patents, analyzed titanium, zirconium, and hafnium nitride films deposited by binary CVD reactions using $\text{Ti}(\text{NMe}_2)_4$, $\text{Zr}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NEt}_2)_4$, respectively. Ex.1034 (IPR2017-00662), p. 9 (Table I); Ex.1032 (IPR2017-00663), p. 9; Ex.1022 (IPR2017-00664), p. 9. The resulting zirconium and hafnium nitride films contained less than 1% carbon and oxygen impurities at all deposition temperatures, and the titanium nitride films contained less than 1% carbon and oxygen impurities when deposited at 200°C. *Id.*, pp. 9-10. Dr. Gordon also obtained a prior art patent in which he disclosed a binary CVD reaction for depositing TiN using tetrakis(dimethylamino) titanium and ammonia, reporting less than 1% carbon and oxygen impurities in the resulting film. 911 Patent, 3:45-4:21.

17. Importantly, this observation that binary reactions result in pure films is not limited to metal nitrides. Dr. Gordon, for example, was issued a prior art patent in which he discloses that one method for reducing carbon and nitrogen contamination in CVD deposition of metal oxide films "is to add an oxidant, such as oxygen or ozone" to the metal precursor vapor. 401 Patent, 1:25-27. That patent goes on to disclose "depositing metal oxides having high purity, not contaminated by elements remaining from the metal ligands, such as carbon, nitrogen, or chlorine," using metal dialkylamide precursors. *Id.*, 1:67-2:2, 2:29-31. Importantly, this also contradicts Dr. Gladfelter's claim that the nitrogen atom found in metal dialkylamides would act as a source of nitrogen contamination when depositing metal oxides. Bastianini, which deposited zirconium oxide from tetrakis(diethylamino)zirconium and oxygen, likewise observed that the resulting zirconium oxide film was of "excellent quality." Bastianini, p. 17. Similarly, the Kamiyama paper cited by Dr. Gladfelter shows that at properly optimized ALD process conditions, hafnium oxide films deposited from a hafnium dialkylamide precursor produced films "suitable" for ultrathin gate dielectric applications that exhibited "remarkably reduced" levels of impurities. Kamiyama, pp. 3-4. Nor would a POSA have considered the use of an inert organic solvent (*e.g.*, as in the grounds based on Buchanan) to be a particular risk for carbon contamination, because Buchanan expressly teaches that the inert liquid need not be co-vaporized

with the metal precursor and may, instead, be diverted from the reactor in liquid form. Buchanan, 7:46-51.

18. I understand that Harvard and Dr. Gladfelter, in discussing the Min reference, suggested that ammonia, specifically, is required to avoid carbon contamination when using metal dialkylamides. See, e.g., Patent Owner Response (IPR2017-00663), at pp. 56-57; Patent Owner Response (IPR2017-00664), at p. 47. In my opinion, this is not how a POSA would have understood Min, especially in view of the references and teachings discussed in the prior paragraph. Rather, as discussed above, a POSA would have understood that a second precursor helps to avoid carbon contamination, but the precursor does not specifically have to be ammonia—or even a nitrogen source. For example, as discussed above, an oxidant such as oxygen or ozone can avoid contamination in reactions where an oxygen source is required to deposit a metal oxide film. 401 Patent, 1:25-27, 1:67-2:2, 2:29-31.

19. A POSA also would not have expected significant nitrogen incorporation into metal oxide films deposited from binary reactions using metal dialkylamides based on the relative strengths of the metal-nitrogen and nitrogen-carbon bonds. As I noted above, bond strength data for common bonds can be readily found in the CRC Handbook of Chemistry and Physics. For example, the 1998-1999 edition of the handbook discloses that a nitrogen-zirconium bond has a

strength of about 564.8 kJ/mol, while a nitrogen-carbon bond has a strength of about 754.3 kJ/mol. CRC Handbook, pp. 4, 7. Because the N-C bond is stronger than the N-Zr bond, a POSA would expect that the N-Zr bond would break more readily, resulting in preferential deposition of zirconium atoms *without* attached nitrogen atoms when a zirconium dialkylamide is used in ALD, which decreases the risk of nitrogen incorporation into the resulting film.

20. Additionally, I note that zirconium and hafnium *oxynitride* films (*i.e.*, films that contain zirconium or hafnium, with bonds to both oxygen atoms and nitrogen atoms) were also known in the art to be insulators. U.S. Patent No. 6,013,553, for example, which issued on January 11, 2000, disclosed the use of zirconium and hafnium oxynitrides as a gate dielectric. 553 Patent, Abstract. Thus, a POSA would have recognized that the potential inclusion of small amounts of nitrogen into an oxygen-containing insulating film deposited using a zirconium or hafnium dialkylamide would not have detracted from the film's usefulness as an insulator. Zirconium and hafnium oxynitride films deposited by ALD using a metal alkylamide precursor meet the "wherein said insulator" claim limitation, because they contain oxygen and the metal atom derived from the metal alkylamide precursor. Thus, the potential inclusion of some nitrogen into such films would not have deterred a POSA from using a metal alkylamide in ALD to arrive at the process claimed in the challenged claims of the 016 Patent.

IV. OPINIONS RELATING TO 539 PATENT BASED ON BUCHANAN

21. My opinions regarding the grounds of invalidity relating to Buchanan were fully set forth in my respective initial declarations in each of the proceedings. I note, based on my review of Harvard's Patent Owner Responses and Dr. Gladfelter's supporting declarations, that Harvard and Dr. Gladfelter have not rebutted many of the opinions I originally provided. As such, the opinions I offer in this declaration are limited to those instances where Harvard's positions raise new issues that I did not address in my original declarations.

22. Both Harvard and Dr. Gladfelter devote much discussion to disputing whether various precursors disclosed in Buchanan could be used in ALD. These precursors are identified in, for example, Ex.2116, ¶¶47-110 in IPR2017-00662. I note, however, that none of these precursors is a zirconium or hafnium precursor that Buchanan identifies as "highly preferred." In fact, none of these precursors contains zirconium or hafnium at all.

A. The Challenged Claims Of The 539 Patent Do Not Require Self-Limiting ALD

23. I understand from reviewing Dr. Gladfelter's deposition testimony that he based his opinions regarding the claims of the 539 Patent on the assumption that the claims require "self-limiting ALD." Gladfelter Tr., at 39:4-9. In my opinion, this is incorrect. As I noted in my opening declarations, ALD reactions

can be made self-limiting by optimizing the process conditions. *See, e.g.*, Ex.1003 (IPR2017-00662), ¶44; Ex.1003 (IPR2017-00663), ¶44; Ex.1003 (IPR2017-00664), ¶44. This optimization is not required, however, and not all ALD processes are self-limiting.

24. Dr. Gladfelter's erroneous interpretation of the claims is also contradicted by the prosecution history of the 016 Patent. I understand from my review of the 016 Patent's file history that during prosecution, the Examiner rejected the then-pending claims of the 016 Patent for obviousness-type double patenting over claims 24-31 of the 539 Patent in view of Vaartstra. Ex.1009 (IPR2017-00662), at p. 6. To overcome this rejection, PO amended the claims of the 016 Patent to expressly require that "deposition of the first reactant component and the second reactant component are self-limiting." *Id.* at pp. 18, 20. In other words, PO represented that the distinguishing feature of the 016 Patent claims, as compared to the 539 Patent claims, is the addition of the "self-limiting" requirement. I therefore understand that the challenged claims of the 539 Patent do not include this requirement, contrary to Dr. Gladfelter's interpretation.

B. Buchanan Expressly Discloses Using A Metal Dialkylamide In Example 3

25. My opinions regarding how Buchanan expressly discloses using its highly preferred zirconium and hafnium dialkylamide precursors in Example 3's

ALD process were set forth in my opening declarations. See Ex.1003 (IPR2017-00662), ¶¶141-144; Ex.1003, (IPR2017-00663), ¶¶118, 122, 142. The additional opinions below simply reasonably elaborate upon the opinions in my opening declarations, as necessary to address new issues raised by PO and Dr. Gladfelter.

26. Buchanan clearly discloses hafnium and zirconium dialkylamide precursors. Buchanan, 14:55-58. These precursors include tetrakis(diethylamino) zirconium ($\text{Zr}(\text{NEt}_2)_4$), tetrakis(diethylamino) hafnium ($\text{Hf}(\text{NEt}_2)_4$), tetrakis(dimethylamino) zirconium ($\text{Zr}(\text{NMe}_2)_4$), and tetrakis(dimethylamino) hafnium ($\text{Hf}(\text{NMe}_2)_4$). *Id.* Buchanan further identifies these four zirconium and hafnium dialkylamides as being "highly preferred." *Id.*

27. Buchanan clearly also discloses, in Example 3, an ALD process to form a "film containing Zr and Hf." Buchanan, 19:60-20:6. Buchanan expressly teaches that this process "can be expanded to include growth of any single component metal, metal oxide, metal nitride, or metal silicide film deposited by atomic layer deposition utilizing one precursor source mixture which contains only one precursor." *Id.*, 20:63-67. In other words, rather than depositing a film containing *both* zirconium and hafnium, Example 3 could be used to deposit a film containing *only* zirconium or *only* hafnium by using a suitable precursor source mixture that contained only a zirconium precursor or only a hafnium precursor, respectively.

28. As I noted above, although PO and Dr. Gladfelter make arguments about whether *other* precursors in Buchanan would have been suitable for ALD, they do not make any arguments that the four highly preferred zirconium and hafnium dialkylamide precursors would have been unsuitable for ALD. *See, e.g.*, Patent Owner Response (IPR2017-00662), at pp. 15-32; Ex.2116 (IPR2017-00662), ¶¶44-110. A POSA would have understood that $\text{Zr}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ are, in fact, suitable for ALD, and therefore would have understood Buchanan to expressly disclose using these precursors in Example 3's ALD process. A POSA would have known that these metal dialkylamides were suitable for ALD for the reasons I discussed in Section III.C, including that they were known to be highly reactive, volatile, and thermally stable against decomposition. *See, e.g.*, Ex.1003 (IPR2017-00662), ¶¶57, 62-63; Bradley II, p. 5; Tsyganova, p. 6; Vaartstra, 4:65-5:12, 5:54-57; Ex.1034 (IPR2017-00662), at pp. 6-7. As noted in Section III.C, a POSA reviewing the file history of the 016 Patent and the Jones paper that Harvard submitted therein would have concluded that Harvard, in representing to the USPTO that the Jones article was indicative of the state of the art, was in agreement with Jones that these properties indicate "the appropriate physical properties and *suitable* deposition chemistry" of ALD precursors. Jones, at p. 2. This is also consistent with what a POSA would have understood in terms of the suitability of ALD precursors.

C. A POSA Would Have At Once Envisaged Using Buchanan's Highly Preferred Metal Dialkylamides In Example 3

29. My opinions regarding how a POSA would have at once envisaged using Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in Example 3's ALD process were set forth in my opening declaration. See Ex.1003 (IPR2017-00662), ¶¶141-144. The additional opinions below simply reasonably elaborate upon the opinions in my opening declarations, as necessary to address new issues raised by PO and Dr. Gladfelter.

30. PO and Dr. Gladfelter appear to argue that, because not all of Buchanan's precursors could be used in Example 3's ALD process, a POSA also would not have at once envisaged specifically using Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in Example 3's ALD process. See, e.g., Patent Owner Response (IPR2017-00662), at pp. 15-32. In my opinion, this ignores how a POSA would have understood Buchanan's teachings.

31. As I noted above, Example 3's ALD process is specifically directed to forming films containing zirconium and hafnium. Buchanan, 19:60-20:6. Buchanan expressly teaches that this process "can be expanded to include growth of any single component metal, metal oxide, metal nitride, or metal silicide film deposited by atomic layer deposition utilizing one precursor source mixture which contains only one precursor." *Id.*, 20:63-67. Additionally, Buchanan discloses that

alkoxides and nitrates, such as hafnium tert-butoxide ($\text{Hf}(\text{O}^t\text{Bu})_4$) and zirconium nitrate ($\text{Zr}(\text{NO}_3)_4$)—the exemplary precursors used in Example 3—had undesirable characteristics. Alkoxides, for example, “are particularly sensitive to water and oxygen impurities” and “may exist in a number of isomeric forms which interconvert over time resulting in a variable vapor pressure.” *Id.*, 2:23-44. Additionally, some alkoxides “are known to change their chemical state by ligand rearrangement, hydrolysis, oligomerization, ring formation, cluster formation, and/or oxidation over time.” *Id.* Nitrates, including zirconium nitrate, “are air and water sensitive and are known to decompose at temperatures around 100°C.” *Id.*, 2:49-53. These teachings in Buchanan are consistent with what was reported elsewhere in the prior art, of which a POSA would have been aware. For example, Leskelä II described alkoxides as having “a tendency to decompose at high temperatures.” Leskelä II, p. 19. Bastianini similarly noted that “in particular alkoxides are very sensitive to hydrolysis.” Bastianini, p. 17. To overcome this shortcoming with alkoxide precursors, Bastianini selected $\text{Zr}(\text{NEt}_2)_4$, a zirconium dialkylamide. *Id.* These teachings, taken together, would have directed a POSA to take up Buchanan’s invitation to expand Example 3 using precursors other than alkoxides and nitrates.

32. Because of the teachings above, a POSA reading Example 3 would therefore have focused on Buchanan’s other precursors that contain zirconium or

hafnium, in order to identify replacements for $\text{Hf}(\text{O}^t\text{Bu})_4$ and $\text{Zr}(\text{NO}_3)_4$. A POSA would *not* have focused on precursors that did not contain zirconium or hafnium, because it would have been clear to a POSA that such precursors could not be used to deposit films containing zirconium and hafnium as per Example 3. As I noted above, none of the precursors that PO and Dr. Gladfelter criticized as being unsuited for ALD is a zirconium-containing or hafnium-containing precursor.

33. Also as noted above, $\text{Zr}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ are specifically identified by Buchanan as being "highly preferred." Buchanan, 14:55-58. Only 27 other zirconium and hafnium precursors are similarly designated by Buchanan, as shown in the list below (which is reproduced from the Petition in IPR2017-00662, at page 48):

- $\text{Cp}_2\text{Me}_2\text{Zr}$ (Buchanan at 9:45, 10:56, 11:60)
- Tetra-methoxy, tetra-ethoxy, tetra-isopropoxy, tetra-tert-butoxy, tetra-iso-butoxy, tetra-butoxy, tetra- $\text{OCH}(\text{CF}_3)_2$, tetra- $\text{OCMe}_2(\text{CF}_3)$, tetra- $\text{OCMe}(\text{CF}_3)_2$, tetra- $\text{OC}(\text{CH}_3)_3$, tetra- $\text{OC}(\text{SiMe}_3)_3$, tetra- $\text{OC}(\text{CF}_3)_3$, or tetra- $\text{OSi}(\text{CH}_3)_3$ Zr or Hf (*id.*, 13:59-63);
- Tetrakis(dimethylamino) Zr or Hf (*id.*, 14:56-57)
- Tetrakis(diethylamino) Zr or Hf (*id.*, 14:57)

34. Of these 31 highly preferred zirconium and hafnium precursors, 26 of them—those listed in the second bullet—are alkoxides or alkoxide derivatives, because they contain a metal-oxygen-carbon bonding structure between the metal atom and each ligand. Tetra-methoxy Zr, for example, consists of a zirconium atom bonded to 4 methoxy (OCH₃) ligands. The zirconium atom is bonded to the oxygen atom, and the oxygen atom is further bonded to a methyl (CH₃) group to yield a metal-oxygen-carbon sequence: Zr-[O-CH₃]₄. A POSA would therefore have understood that these 26 precursors are prone to the same suboptimal properties of alkoxides that Buchanan and the prior art disclosed, as discussed above. Accordingly, a POSA would have focused on the remaining 5 highly preferred precursors, of which 4 are zirconium and hafnium dialkylamides (*i.e.*, the last 2 bullets in the list above).

35. Because Buchanan's teachings would have directed a POSA to Buchanan's narrow and finite list of 31 highly preferred zirconium and hafnium precursors, and within that list, further directed a POSA to the 5 non-alkoxide precursors (of which 4 are dialkylamides), in the manner discussed above, in my opinion a POSA would have at once envisaged using those members of the list in Example 3's ALD process.

D. It Would Have Been Obvious To A POSA To Use A Metal Dialkylamide Precursor With Example 3

36. My opinions regarding why a POSA would have found it obvious to use Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in Example 3's ALD process were set forth in my opening declarations. See Ex.1003 (IPR2017-00662), ¶¶132-170; Ex.1003, (IPR2017-00663), ¶¶142-147. The additional opinions below simply reasonably elaborate upon the opinions in my opening declarations, as necessary to address new issues raised by PO and Dr. Gladfelter.

37. The Patent Owner Responses assert that Micron did not explain why a POSA would have chosen to use a metal dialkylamide precursor in Example 3's ALD process. See, e.g., Patent Owner Response (IPR2017-00662), at pp. 44-46; Patent Owner Response (IPR2017-00663), at pp. 27-29. I disagree. As I indicated above, my initial declarations set forth numerous motivations that a POSA would have had to use a metal dialkylamide precursor in Example 3, all of which would have directed a POSA to Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in particular.

38. As I noted above, Example 3's ALD process is specifically directed to forming films containing zirconium and hafnium. Buchanan, 19:60-20:6. Buchanan expressly teaches that this process "can be expanded to include growth of any single component metal, metal oxide, metal nitride, or metal silicide film deposited by atomic layer deposition utilizing one precursor source mixture which

contains only one precursor." *Id.*, 20:63-67. Additionally, Buchanan discloses that alkoxides and nitrates, such as hafnium tert-butoxide ($\text{Hf}(\text{O}^t\text{Bu})_4$) and zirconium nitrate ($\text{Zr}(\text{NO}_3)_4$)—the exemplary precursors used in Example 3—had undesirable characteristics. Alkoxides, for example, "are particularly sensitive to water and oxygen impurities" and "may exist in a number of isomeric forms which interconvert over time resulting in a variable vapor pressure." *Id.*, 2:23-44. Additionally, some alkoxides "are known to change their chemical state by ligand rearrangement, hydrolysis, oligomerization, ring formation, cluster formation, and/or oxidation over time." *Id.* Nitrates, including zirconium nitrate, "are air and water sensitive and are known to decompose at temperatures around 100°C." *Id.*, 2:49-53. These teachings in Buchanan are consistent with what was reported elsewhere in the prior art, of which a POSA would have been aware. For example, Leskelä II described alkoxides as having "a tendency to decompose at high temperatures." Leskelä II, p. 19. Bastianini similarly noted that "in particular alkoxides are very sensitive to hydrolysis." Bastianini, p. 17. To overcome this shortcoming with alkoxide precursors, Bastianini selected $\text{Zr}(\text{NEt}_2)_4$, a zirconium dialkylamide, to form a metal oxide through a binary CVD reaction. *Id.* These teachings, taken together, would have directed a POSA to take up Buchanan's invitation to use precursors in Example 3 other than alkoxides and nitrates.

39. Because of the teachings above, a POSA reading Example 3 would therefore have focused on Buchanan's precursors that contain zirconium or hafnium, in order to identify replacements for $\text{Hf}(\text{O}^t\text{Bu})_4$ and $\text{Zr}(\text{NO}_3)_4$. A POSA would *not* have focused on precursors that did not contain zirconium or hafnium, because it would have been clear to a POSA that such precursors could not be used to deposit films containing zirconium and hafnium as per Example 3. As I noted above, none of the precursors that PO and Dr. Gladfelter criticized as being unsuited for ALD is a zirconium-containing or hafnium-containing precursor.

40. Also as noted above, $\text{Zr}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ are specifically identified by Buchanan as being "highly preferred." Buchanan, 14:55-58. Only 27 other zirconium and hafnium precursors are similarly designated by Buchanan, as shown in the list below (which is reproduced from the Petition in IPR2017-00662, at p. 48):

- $\text{Cp}_2\text{Me}_2\text{Zr}$ (Buchanan at 9:45, 10:56, 11:60)
- Tetra-methoxy, tetra-ethoxy, tetra-isopropoxy, tetra-tert-butoxy, tetra-iso-butoxy, tetra-butoxy, tetra- $\text{OCH}(\text{CF}_3)_2$, tetra- $\text{OCMe}_2(\text{CF}_3)$, tetra- $\text{OCMe}(\text{CF}_3)_2$, tetra- $\text{OC}(\text{CH}_3)_3$, tetra- $\text{OC}(\text{SiMe}_3)_3$, tetra- $\text{OC}(\text{CF}_3)_3$, or tetra- $\text{OSi}(\text{CH}_3)_3$ Zr or Hf (*id.*, 13:59-63);
- Tetrakis(dimethylamino) Zr or Hf (*id.*, 14:56-57)

- Tetrakis(diethylamino) Zr or Hf (*id.*, 14:57)

41. Of these 31 highly preferred zirconium and hafnium precursors, 26 of them—those listed in the second bullet—are alkoxides or alkoxide derivatives, because they contain a metal-oxygen-carbon bonding structure between the metal atom and each ligand. Tetra-methoxy Zr, for example, consists of a zirconium atom bonded to 4 methoxy (OCH₃) ligands. The zirconium atom is bonded to the oxygen atom, and the oxygen atom is further bonded to a methyl (CH₃) group to yield a metal-oxygen-carbon sequence: Zr-[O-CH₃]₄. A POSA would therefore have understood that these 26 precursors are prone to the same suboptimal properties of alkoxides that Buchanan and the prior art disclosed, as discussed above. Accordingly, a POSA would have further focused on the remaining 5 highly preferred precursors, of which 4 are zirconium and hafnium dialkylamides (*i.e.*, the last 2 bullets in the list above).

42. Because Buchanan's teachings would have directed a POSA to such a narrow and finite list of highly preferred zirconium and hafnium precursors in the manner discussed above, in my opinion a POSA would have been motivated to use Buchanan's highly preferred zirconium and hafnium dialkylamides in Example 3's ALD process.

43. Further, a POSA would have had a reasonable expectation of success. As I discussed above, Bastianini selected a zirconium dialkylamide precursor for binary CVD to overcome the problems associated with alkoxide precursors. Bastianini, p. 17. As I discussed in Section III.E, a POSA would have understood and expected from the teachings of the prior art that binary CVD had been used to deposit metal oxide films that were of high quality, with low levels of impurities. *Id.*; 401 Patent, 1:66-2:2, 2:29-31; Vaartstra, 6:21-56, 11:8-10. Further, as discussed in Section III.A, a POSA would have understood from the prior art that the success of metal dialkylamide precursors in binary CVD reactions would generally predict whether those same precursors would be effective in ALD reactions. George, p. 5; Leskelä II, p. 15; Putkonen (Ex.1068 (IPR2017-00662); Ex.1066 (IPR2017-00663); Ex.1064 (IPR2017-00664)), p. 1. The fact that zirconium and hafnium are in the same column of the periodic table as titanium would also have provided a POSA with a reasonable expectation of success, because titanium dialkylamides such as TEMAT, $\text{Ti}(\text{NEt}_2)_4$, $\text{Ti}(\text{NME}_2)_4$, and $\text{Ti}(\text{N}^i\text{PrMe})_4$ had all been described for use in ALD reactions, as reported in Min and Leskelä 865. Min, p. 7; Leskelä 865, 7:6-23; Gladfelter Tr., at 209:10-23, 223:19-222:4.

**1. A POSA Would Not Have Limited His Choice Of
Precursors To Alkoxides And Nitrates**

44. PO and Dr. Gladfelter argue that a POSA, if using different precursors in Example 3, would limit the choice of precursors to other alkoxides and nitrates. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 62. I disagree. As already noted above, Bastianini expressly taught using a metal dialkylamide, tetrakis(diethylamino) zirconium, as a zirconium precursor for depositing zirconium oxide in a binary CVD reaction in order to avoid the shortcomings of alkoxide precursors. Bastianini, p. 17. This would have provided an express teaching, suggestion, or motivation to a POSA to look beyond alkoxides and nitrates, and specifically to look to metal dialkylamides.

45. Additionally, Buchanan identifies no nitrate precursors as "highly preferred." Buchanan, 16:51-55. The only zirconium-containing nitrate precursor that Buchanan identifies is zirconium nitrate— $\text{Zr}(\text{NO}_3)_4$. *Id.*; Gladfelter Tr., at 97:18-23. This precursor is already used in Example 3, and is specifically identified by Buchanan as an example of a nitrate that is undesirably unstable due to being air and water sensitive and having a low decomposition temperature around 100°C. Buchanan, 2:49-53. A POSA would therefore have been unable to find in Buchanan any highly preferred nitrate-containing zirconium precursors to use with Example 3, which would have motivated a POSA to look to Buchanan's other highly preferred zirconium precursors.

2. Buchanan Did Not Teach Away From Metal Dialkylamides

46. PO and Dr. Gladfelter also claim that Buchanan "describes that alkylamides have the same suboptimal chemical characteristics as alkoxides," and that therefore Buchanan teaches away from using metal dialkylamides. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 60; Ex.2101 (IPR2017-00662), ¶¶91; Patent Owner Response (IPR2017-00663), at p. 47; Ex.2101 (IPR2017-00663), ¶¶97. I disagree with this assertion, because it misinterprets and mischaracterizes Buchanan. First of all, the portion of column 2 of Buchanan on which PO and Dr. Gladfelter rely does not even mention "alkylamides," and a POSA would not have understood that portion to pertain to alkylamides. *See* Buchanan, 2:45-46. Instead, a POSA would have understood this statement to describe that amongst the genus of metal amides (*i.e.*, compounds in which a metal atom is bound to a nitrogen atom, with two substituent groups bound to each nitrogen atom), there are metal amides "which behave similarly to alkoxides" in terms of their chemical stability and the characteristics discussed in Buchanan.

47. As I noted above, the alkoxy ligands in metal alkoxides have oxygen-carbon bonds. As Dr. Gladfelter testified in his deposition, some metal amides include oxygen-carbon bonds in the substituent groups of the amino ligands, which make the metal complex more volatile. Gladfelter Tr., at 20:2-22:9. A POSA would therefore have understood that when Buchanan refers to those "amides which behave similarly to alkoxides," Buchanan is referring to specific metal

amides that have chemical structures (oxygen-carbon bonds in the ligands, for example) which result in the metal amides having volatility and thermal stability comparable to alkoxides.

48. The highly preferred zirconium and hafnium alkylamide precursors disclosed in Buchanan, however, do not have such chemical structures. A POSA therefore would not have been deterred from using them in Example 3 by Buchanan's teachings.

3. The Prior Art Did Not Teach Away From Using Metal Dialkylamides

49. PO and Dr. Gladfelter assert that a POSA would have been dissuaded from using metal dialkylamides in ALD because the prior art purportedly gave a POSA reasons to believe that films deposited using metal dialkylamides would be contaminated with carbon and nitrogen. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 63; Patent Owner Response (IPR2017-00663), at p. 50. As I discussed in Section III.E, however, this is not what a POSA would have understood from the prior art and therefore, for the same reasons, a POSA would not have been dissuaded from using metal dialkylamides.

V. OPINIONS RELATING TO 016 PATENT BASED ON BUCHANAN

50. My opinions regarding the grounds of invalidity relating to Buchanan were fully set forth in my respective initial declarations in each of the proceedings.

I note, based on my review of Harvard's Patent Owner Responses and Dr. Gladfelter's supporting declarations, that Harvard and Dr. Gladfelter have not rebutted many of the opinions I originally provided. As such, the opinions I offer in this declaration are limited to those instances where Harvard's positions raise new issues that I did not address in my original declarations.

51. Both Harvard and Dr. Gladfelter devote significant discussion to disputing whether various precursors disclosed in Buchanan could be used in ALD. These precursors are identified in, for example, Ex.2116, ¶¶ 50-115 in IPR2017-00663. I note, however, that none of these precursors is a zirconium or hafnium precursor that Buchanan identifies as "highly preferred." In fact, none of these precursors contains zirconium or hafnium at all.

A. Buchanan Expressly Discloses Using A Metal Dialkylamide In Example 3

52. My opinions regarding how Buchanan expressly discloses using its highly preferred zirconium and hafnium dialkylamide precursors in Example 3's ALD process were set forth in my opening declarations. See Ex.1003 (IPR2017-00662), ¶¶ 141-144; Ex.1003, (IPR2017-00663), ¶¶ 118, 122, 142. The additional opinions below simply reasonably elaborate upon the opinions in my opening declarations, as necessary to address new issues raised by PO and Dr. Gladfelter.

53. Buchanan clearly discloses hafnium and zirconium dialkylamide precursors. Buchanan, 14:55-58. These precursors include tetrakis(diethylamino) zirconium ($\text{Zr}(\text{NEt}_2)_4$), tetrakis(diethylamino) hafnium ($\text{Hf}(\text{NEt}_2)_4$), tetrakis(dimethylamino) zirconium ($\text{Zr}(\text{NMe}_2)_4$), and tetrakis(dimethylamino) hafnium ($\text{Hf}(\text{NMe}_2)_4$). *Id.* Buchanan further identifies these 4 zirconium and hafnium dialkylamides as being "highly preferred." *Id.*

54. Buchanan clearly also discloses, in Example 3, an ALD process to form a "film containing Zr and Hf." Buchanan, 19:60-20:6. Buchanan expressly teaches that this process "can be expanded to include growth of any single component metal, metal oxide, metal nitride, or metal silicide film deposited by atomic layer deposition utilizing one precursor source mixture which contains only one precursor." *Id.*, 20:63-67. In other words, rather than depositing a film containing *both* zirconium and hafnium, Example 3 could be used to deposit a film containing *only* zirconium or *only* hafnium by using a suitable precursor source mixture that contained only a zirconium precursor or only a hafnium precursor, respectively.

55. As I noted above, although PO and Dr. Gladfelter make arguments about whether *other* precursors in Buchanan would have been suitable for ALD, they do not make any arguments that the four highly preferred zirconium and hafnium dialkylamide precursors would have been unsuitable for ALD. A POSA

would have understood that $\text{Zr}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ are, in fact, suitable for ALD, and therefore would have understood Buchanan to expressly disclose using these precursors in Example 3's ALD process. A POSA would have known that these metal dialkylamides were suitable for ALD for the reasons I discussed in Section III.C, including that they were known to be highly reactive, volatile, and thermally stable against decomposition. *See, e.g.*, Ex.1003 (IPR2017-00662), ¶¶57, 62-63; Bradley II, p. 5; Tsyganova, p. 6; Vaartstra, 4:65-5:12, 5:54-57; Ex.1034 (IPR2017-00662), at pp. 6-7. As noted in Section III.C, a POSA reviewing the file history of the 016 Patent and the Jones paper that Harvard submitted therein would have concluded that Harvard, in representing to the USPTO that the Jones article was indicative of the state of the art, was in agreement with Jones that these properties indicate "the appropriate physical properties and *suitable* deposition chemistry" of ALD precursors. Jones, p.2. This is also consistent with what a POSA would have understood in terms of the suitability of ALD precursors.

B. It Would Have Been Obvious To A POSA To Use A Metal Dialkylamide Precursor With Example 3

56. My opinions regarding why a POSA would have found it obvious to use Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in Example 3's ALD process were set forth in my opening declarations. *See*

Ex.1003 (IPR2017-00662), ¶¶132-170; Ex.1003, (IPR2017-00663), ¶¶142-147.

The additional opinions below simply reasonably elaborate upon the opinions in my opening declarations, as necessary to address new issues raised by PO and Dr. Gladfelter.

57. The Patent Owner Responses assert that Micron did not explain why a POSA would have chosen to use a metal dialkylamide precursor in Example 3's ALD process. *See, e.g.*, Patent Owner Response (IPR2017-00662), at pp. 44-46; Patent Owner Response (IPR2017-00663), at pp. 27-29. I disagree. As I indicated above, my initial declarations set forth numerous motivations that a POSA would have had to use a metal dialkylamide precursor in Example 3, all of which would have directed a POSA to Buchanan's highly preferred zirconium and hafnium dialkylamide precursors in particular.

58. As I noted above, Example 3's ALD process is specifically directed to forming films containing zirconium and hafnium. Buchanan, 19:60-20:6. Buchanan expressly teaches that this process "can be expanded to include growth of any single component metal, metal oxide, metal nitride, or metal silicide film deposited by atomic layer deposition utilizing one precursor source mixture which contains only one precursor." *Id.*, 20:63-67. Additionally, Buchanan discloses that alkoxides and nitrates, such as hafnium tert-butoxide ($\text{Hf}(\text{O}^t\text{Bu})_4$) and zirconium nitrate ($\text{Zr}(\text{NO}_3)_4$)—the exemplary precursors used in Example 3—had undesirable

characteristics. Alkoxides, for example, "are particularly sensitive to water and oxygen impurities" and "may exist in a number of isomeric forms which interconvert over time resulting in a variable vapor pressure." *Id.*, 2:23-44. Additionally, some alkoxides "are known to change their chemical state by ligand rearrangement, hydrolysis, oligomerization, ring formation, cluster formation, and/or oxidation over time." *Id.* Nitrates, including zirconium nitrate, "are air and water sensitive and are known to decompose at temperatures around 100°C." *Id.*, 2:49-53. These teachings in Buchanan are consistent with what was reported elsewhere in the prior art, of which a POSA would have been aware. For example, Leskelä II described alkoxides as having "a tendency to decompose at high temperatures." Leskelä II, p. 19. Bastianini similarly noted that "in particular alkoxides are very sensitive to hydrolysis." Bastianini, p. 17. To overcome this shortcoming with alkoxide precursors, Bastianini selected $\text{Zr}(\text{NEt}_2)_4$, a zirconium dialkylamide, for a binary CVD reaction to form a metal oxide film. *Id.* These teachings, taken together, would have directed a POSA to take up Buchanan's invitation to expand Example 3 using precursors other than alkoxides and nitrates.

59. Because of the teachings above, a POSA reading Example 3 would therefore have focused on Buchanan's precursors that contain zirconium or hafnium, in order to identify replacements for $\text{Hf}(\text{O}^i\text{Bu})_4$ and $\text{Zr}(\text{NO}_3)_4$. A POSA would *not* have focused on precursors that did not contain zirconium or hafnium,

because it would have been clear to a POSA that such precursors could not be used to deposit films containing zirconium and hafnium as per Example 3. As I noted above, none of the precursors that PO and Dr. Gladfelter criticized as being unsuited for ALD is a zirconium-containing or hafnium-containing precursor.

60. Also as noted above, $\text{Zr}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ are specifically identified by Buchanan as being "highly preferred." Buchanan, 14:55-58. Only 27 other zirconium and hafnium precursors are similarly designated by Buchanan, as shown in the list below (which is reproduced from the Petition in IPR2017-00662, at page 48):

- $\text{Cp}_2\text{Me}_2\text{Zr}$ (Buchanan at 9:45, 10:56, 11:60)
- Tetra-methoxy, tetra-ethoxy, tetra-isopropoxy, tetra-tert-butoxy, tetra-iso-butoxy, tetra-butoxy, tetra- $\text{OCH}(\text{CF}_3)_2$, tetra- $\text{OCMe}_2(\text{CF}_3)$, tetra- $\text{OCMe}(\text{CF}_3)_2$, tetra- $\text{OC}(\text{CH}_3)_3$, tetra- $\text{OC}(\text{SiMe}_3)_3$, tetra- $\text{OC}(\text{CF}_3)_3$, or tetra- $\text{OSi}(\text{CH}_3)_3$ Zr or Hf (*id.*, 13:59-63);
- Tetrakis(dimethylamino) Zr or Hf (*id.*, 14:56-57)
- Tetrakis(diethylamino) Zr or Hf (*id.*, 14:57)

61. Of these 31 highly preferred zirconium and hafnium precursors, 26 of them—those listed in the second bullet—are alkoxides or alkoxide derivatives, because they contain a metal-oxygen-carbon bonding structure between the metal

atom and each ligand. Tetra-methoxy Zr, for example, consists of a zirconium atom bonded to 4 methoxy (OCH₃) ligands. The zirconium atom is bonded to the oxygen atom, and the oxygen atom is further bonded to a methyl (CH₃) group to yield a metal-oxygen-carbon sequence: Zr-[O-CH₃]₄. A POSA would therefore have understood that these 26 precursors are prone to the same suboptimal properties of alkoxides that Buchanan and the prior art disclosed, as discussed above. Accordingly, a POSA would have further focused on the remaining 5 highly preferred precursors, of which 4 are zirconium and hafnium dialkylamides (*i.e.*, the last 2 bullets in the list above).

62. Because Buchanan's teachings would have directed a POSA to such a narrow and finite list of highly preferred zirconium and hafnium precursors in the manner discussed above, in my opinion a POSA would have been motivated to use Buchanan's highly preferred zirconium and hafnium dialkylamides in Example 3's ALD process.

63. Further, a POSA would have had a reasonable expectation of success. As I discussed in above, Bastianini selected a zirconium dialkylamide precursor for use in a binary CVD reaction to form a metal oxide film to overcome the problems associated with alkoxide precursors. Bastianini, p. 17. As I discussed in Section III.E, a POSA would have understood and expected from the teachings of the prior art that binary CVD had been used to deposit metal oxide

films that were of high quality, with low levels of impurities. *Id.*; 401 Patent, 1:66-2:2, 2:29-31; Vaartstra, 6:21-56, 11:8-10. Further, as discussed in Section III.A, a POSA would have understood from the prior art that the success of metal dialkylamide precursors in binary CVD reactions would generally predict whether those same precursors would be effective in ALD reactions. George, p. 5; Leskelä II, p. 15; Putkonen (Ex.1068 (IPR2017-00662); Ex.1066 (IPR2017-00663); Ex.1064 (IPR2017-00664)), p. 1. The fact that zirconium and hafnium are in the same column of the periodic table as titanium would also have provided a POSA with a reasonable expectation of success, because titanium dialkylamides such as TEMAT, $\text{Ti}(\text{NEt}_2)_4$, $\text{Ti}(\text{NME}_2)_4$, and $\text{Ti}(\text{N}^i\text{PrMe})_4$ had all been described for use in ALD reactions, as reported in Min and Leskelä 865. Min, p. 7; Leskelä 865, 7:6-23; Gladfelter Tr., at 209:10-23, 223:19-222:4.

1. A POSA Would Not Have Limited His Choice Of Precursors To Alkoxides And Nitrates

64. PO and Dr. Gladfelter argue that a POSA, if using different precursors in Example 3, would limit the choice of precursors to other alkoxides and nitrates. *See, e.g.*, Patent Owner Response (IPR2017-00663), at pp. 48-49. I disagree. As already noted above, Bastianini expressly taught using a metal dialkylamide, tetrakis(diethylamino) zirconium, as a zirconium precursor for depositing zirconium oxide in a binary CVD reaction in order to avoid the shortcomings of

alkoxide precursors. Bastianini, 17. This would have provided an express teaching, suggestion, or motivation to a POSA to look beyond alkoxides and nitrates, and specifically to look to metal dialkylamides.

65. Additionally, Buchanan identifies no nitrate precursors as "highly preferred." Buchanan, 16:51-55. The only zirconium-containing nitrate precursor that Buchanan identifies is zirconium nitrate— $\text{Zr}(\text{NO}_3)_4$. *Id.*; Gladfelter Tr., at 97:18-23. This precursor is already used in Example 3, and is specifically identified by Buchanan as an example of a nitrate that is undesirably unstable due to being air and water sensitive and having a low decomposition temperature around 100°C. Buchanan, 2:49-53. A POSA would therefore have been unable to find in Buchanan any highly preferred nitrate-containing zirconium precursors to use with Example 3, which would have motivated a POSA to look to Buchanan's other highly preferred zirconium precursors.

2. Buchanan Did Not Teach Away From Metal Dialkylamides

66. PO and Dr. Gladfelter also claim that Buchanan "describes that alkylamides have the same suboptimal chemical characteristics as alkoxides," and that therefore Buchanan teaches away from using metal dialkylamides. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 60; Ex.2101 (IPR2017-00662), ¶91; Patent Owner Response (IPR2017-00663), at p. 47; Ex.2101 (IPR2017-00663), ¶97. I disagree with this assertion, because it misinterprets and

mischaracterizes Buchanan. First of all, the portion of column 2 of Buchanan on which PO and Dr. Gladfelter rely does not even mention "alkylamides," and a POSA would not have understood that portion to pertain to alkylamides. See Buchanan, 2:45-46. Instead, a POSA would have understood this statement to describe that amongst the genus of metal amides (*i.e.*, compounds in which a metal atom is bound to a nitrogen atom, with two substituent groups bound to each nitrogen atom), there are metal amides "which behave similarly to alkoxides" in terms of their chemical stability and the characteristics discussed in Buchanan.

67. As I noted above, the alkoxy ligands in metal alkoxides have oxygen-carbon bonds. As Dr. Gladfelter testified in his deposition, some metal amides include oxygen-carbon bonds in the substituent groups of the amino ligands, which make the metal complex more volatile. Gladfelter Tr., at 20:2-22:9. A POSA would therefore have understood that when Buchanan refers to those "amides which behave similarly to alkoxides," Buchanan is referring to specific metal amides that have chemical structures (oxygen-carbon bonds in the ligands, for example) which result in the metal amides having volatility and thermal stability comparable to alkoxides.

68. The highly preferred zirconium and hafnium alkylamide precursors disclosed in Buchanan, however, do not have such chemical structures. A POSA

therefore would not have been deterred from using them in Example 3 by Buchanan's teachings.

3. The Prior Art Did Not Teach Away From Using Metal Dialkylamides

69. PO and Dr. Gladfelter assert that a POSA would have been dissuaded from using metal dialkylamides in ALD because the prior art purportedly gave a POSA reasons to believe that films deposited using metal dialkylamides would be contaminated with carbon and nitrogen. *See, e.g.*, Patent Owner Response (IPR2017-00662), at p. 63; Patent Owner Response (IPR2017-00663), at p. 50. As I discussed in Section III.E, however, this is not what a POSA would have understood from the prior art and therefore, for the same reasons, a POSA would not have been dissuaded from using metal dialkylamides.

C. It Would Have Been Obvious To A POSA To Combine Buchanan With Min

70. My opinions regarding why a POSA would have found it obvious to apply Min's procedure for identifying an ALD window and optimizing an ALD process to be self-limiting to Buchanan's Example 3 were set forth in my initial declaration in IPR2017-00663. *See* Ex.1003, (IPR2017-00663), ¶¶ 148-155. The additional opinions below simply reasonably elaborate upon the opinions in my opening declaration, as necessary to address new issues raised by PO and Dr. Gladfelter.

71. PO and Dr. Gladfelter argue that a POSA would not have had a reasonable expectation of success in combining Buchanan with Min in this way because Min's teachings, according to PO and Dr. Gladfelter, are limited to the specific context of an ALD reaction using TEMAT and ammonia to deposit titanium nitride. Patent Owner Response (IPR2017-00663), at pp. 54-55. I disagree.

72. As an initial matter, I do not understand the Petition to assert that a POSA would have applied the exact process conditions used in Min to Buchanan's Example 3, and that is not the obviousness combination that I opined on in my opening declaration. Rather, in my opinion, a POSA would have found it obvious to take the *broader teaching* in Min of a procedure for identifying the self-limiting ALD window for a given ALD process—regardless of what precursors that process uses—and apply that procedure to Buchanan's Example 3 in order to identify the process conditions for self-limiting deposition when using Buchanan's highly preferred metal dialkylamide precursors. As I discussed in Section III.B, the general procedure taught in Min was routine and within the abilities of a POSA, and was commonly applied in this field to optimize ALD process conditions and determine the breadth of the self-limiting ALD window. I have seen no evidence in PO's Patent Owner Responses, expert declarations, or exhibits to suggest that the procedure would have been inapplicable outside of Min's TEMAT/NH₃

reaction. Additionally, while PO suggests that a POSA would not have been able to predict whether applying a procedure such as Min's to a new precursor would actually yield an available ALD window, using tetramethylsilane as an example of a compound with no ALD window (Patent Owner Response (IPR2017-00663), at p. 54), I do not understand the grounds in the Petition to assert invalidity based on a reaction involving tetramethylsilane. Based on my review of the Patent Owner Responses and supporting evidence, I note that PO has not disputed that the highly preferred zirconium and hafnium dialkylamides disclosed in Buchanan— $\text{Zr}(\text{NEt}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, and $\text{Hf}(\text{NMe}_2)_4$ —have an available ALD window. $\text{Hf}(\text{NMe}_2)_4$, for example, exhibits self-limiting behavior in the ALD deposition of hafnium oxide at 300°C, indicating that a suitable window for that precursor exists. Inman, pp. 2-3.

73. Additionally, the prior art teaches that the same metal dialkylamide precursor can be used to deposit both oxide films and nitride films by making an appropriate choice of the second reactant. Indeed, Buchanan itself expressly discloses this in connection with Example 3. Buchanan, 20:16-24. For example, a nitride film would require a second reactant that contributes nitrogen atoms, such as ammonia, hydrazine, hydrogen azide, or tertbutylamine, among other possibilities. *Id.*, 20:20-24. An oxide film using the same metal precursor would require a second reactant that contributes oxygen atoms, such as oxygen, ozone,

water, hydrogen peroxide, or nitrous oxide. *Id.*, 20:16-20. Thus, a POSA would not have understood Min to be inapplicable to the deposition of oxygen-containing metal films simply because the specific example used in Min was the deposition of a titanium nitride.

VI. OPINIONS RELATING TO GROUNDS BASED ON SENZAKI

74. My opinions regarding the grounds of invalidity relating to Senzaki were fully set forth in my initial declaration. I note, based on my review of the Patent Owner Response and Dr. Gladfelter's supporting declaration, that PO and Dr. Gladfelter have not rebutted many of the opinions I originally provided. As such, the opinions I offer in this declaration are limited to those instances where PO's positions raise new issues that I did not address in my original declaration.

A. Senzaki Discloses An ALD Process Using $\text{Zr}(\text{NEt}_2)_4$

75. PO and Dr. Gladfelter assume that Senzaki does not disclose an ALD process using $\text{Zr}(\text{NEt}_2)_4$, arguing that Senzaki does not describe what precursors are suitable for ALD. POR at 24-29; Ex.2120 (IPR2017-00664), ¶¶ 60-70. I disagree. Senzaki expressly discloses an ALD process using a metal alkylamide ($\text{Zr}(\text{NEt}_2)_4$). Thus, it is unnecessary to look at suitability, though as I describe in Sections III.A.-E., it was known that metal alkylamides were suitable for ALD processes, that using metal alkylamides in ALD processes was not unpredictable,

that it was routine to dial in ALD processes to be self-limiting, and that issues such as contamination were not deterrents.

76. Senzaki clearly discloses an ALD process using $\text{Zr}(\text{NEt}_2)_4$. $\text{Zr}(\text{NEt}_2)_4$ is a metal alkylamide. Ex.1003, (IPR2017-00664) ¶39. Senzaki discloses " $\text{Zr}(\text{NEt}_2)_4$ " as exemplifying the invention when it initially describes an exemplary process. Senzaki, 3:40-43. By specifically pointing out this precursor by name (not a general formula referring to many different precursors), and stating that it exemplifies the invention, a POSA would have understood this metal alkylamide to be a key precursor of interest to Senzaki. Then, shortly after this, Senzaki states that the "above precursors could be used for" ALD. *Id.* at 4:4-15. Not only is $\text{Zr}(\text{NEt}_2)_4$ one of the "above precursors," it is the one metal precursor that Senzaki specifically calls out by name. Thus, Senzaki discloses an ALD process that uses $\text{Zr}(\text{NEt}_2)_4$ as a precursor.

77. Dr. Gladfelter appears to argue that a POSA would have done experimentation to confirm that $\text{Zr}(\text{NEt}_2)_4$ would be suitable for ALD. Ex.2120 (IPR2017-00664), ¶164. I disagree, because Senzaki expressly describes an ALD process using $\text{Zr}(\text{NEt}_2)_4$. Regardless, it was routine for a POSA to conduct a confirming experiment of a vapor phase reaction, even when there was a high expectation that the reaction would work. Here, the experimentation would be routine, effectively turning a knob to adjust substrate temperature. Again, it was

known that metal alkylamides were suitable for ALD processes, that using metal alkylamides in ALD processes was not unpredictable, and that it was routine to dial in ALD processes to be self-limiting (effectively adjusting the temperature). See Sections III.A-D.

78. Dr. Gladfelter also asserts that Senzaki does not disclose the deposition conditions for its ALD process. Ex.2120 (IPR2017-00664), ¶166. My opening declaration details how routine it was to dial in an ALD process to be "self-limiting," i.e., to determine the deposition conditions for self-limiting ALD. Ex.1003, (IPR2017-00664), ¶¶130-37. I further address this in Section III.B.

B. Senzaki Discloses ALD Processes That Include And That Do Not Include A Compositional Gradient

79. PO and Dr. Gladfelter argue that a POSA would not have found it obvious to use an ALD process with Senzaki's teachings, because Senzaki teaches achieving a compositional gradient. POR at 29-35; Ex.2120 (IPR2017-00664), ¶¶171-81. I disagree. Senzaki teaches both an ALD process that does not achieve a compositional gradient (because it does not vary temperature) and an ALD process that does achieve a compositional gradient (because it varies temperature).

80. As an initial matter, Senzaki does not disparage depositing its films without a compositional gradient. Senzaki teaches a deposition process that uses multicomponent metal-containing materials, such as mixed-metal/metalloid oxides,

to produce films such as gate dielectrics. Importantly, Senzaki recognizes that there are advantages to using multicomponent metal-containing materials, such as mixed-metal/metalloid oxides, even though they do not include a compositional gradient. Specifically, Senzaki describes that these materials—without a compositional gradient—“often have unique physical properties that each individual metal/metalloid oxide/nitride component does not possess. For example, some mixed metal oxides can be used for high dielectric constant materials” Senzaki at 1:7-12. Senzaki goes on to cite several references that illustrate this point. *Id.* at 1:12-23.

81. Senzaki then recites some benefits of using a mixed metal/metalloid film in the context of “metal silicates as gate dielectric films,” even though the film does not include a compositional gradient. *Id.* at 1:41-46. There, Senzaki cites Wilk *et. al.*, *Hafnium and Zirconium silicates for advanced gate dielectrics*, Journal of Applied Physics, Vol. 87, No. 1, 2000, pp. 9-17 (“Wilk”). Wilk discloses a ZrSi_xO_y film for a gate dielectric, just like Senzaki. *Id.* at Abstract. Wilk notes that this film enables “excellent” and “very good” results depending on the gate electrode material chosen. *Id.* In short, Wilk recognizes the advantages of a ZrSi_xO_y film for a gate dielectric even though it does not include a compositional gradient.

82. Of course, Senzaki also teaches the use of a compositional gradient in these films. Senzaki states that a compositional gradient is "desirable." Senzaki, 2:20-23. It was known in the art that a gradient is desirable because, for example, having more silicon at the interface with the substrate can minimize scattering of electrons/holes when they flow from source to drain along the channel of a metal oxide semiconductor field effect transistor (MOSFET). Having less silicon (and more of the metal) at the interface with the gate electrode can increase the overall dielectric constant of the gate dielectric, increase gate capacitance, and thus improve MOSFET drain currents.

83. Only after recognizing the advantages of these metal/metalloid films does Senzaki state that a compositional gradient is "desirable." Senzaki, 2:18-28. I agree that achieving a compositional gradient was Senzaki's overarching goal in that he teaches ways to achieve a compositional gradient. But in no way does Senzaki criticize or disparage metal/metalloid films that do not have a compositional gradient. Instead, Senzaki recognizes the benefits of such films, citing several references that confirm their general benefits (see above). And in fact, Senzaki discloses an ALD method that does not change the temperature to achieve a compositional gradient, further confirming that he does not disparage the benefits of metal/metalloid films.

84. Based on the above description, and based on the plain language of the specification, a POSA would have understood Senzaki's ALD disclosure in columns 3 and 4 to include an ALD process that does not vary the temperature to achieve a compositional gradient. Such a process would obtain the benefits of ALD (e.g., more conformal films and greater thickness control) while still retaining the benefits of a metal/metalloid film. As I describe in my opening declaration, thickness control was critical, e.g., for dielectric films such as those in Senzaki. Ex.1003 (IPR2017-00664), ¶¶65-72. Further, Senzaki itself discloses this thickness control and suggests self-limiting deposition by noting that in ALD "an approximately single layer of precursor molecules are adsorbed on a surface." Ex.1003 (IPR2017-00664), at ¶99.

85. Senzaki also discloses an ALD process that varies the temperature to achieve a compositional gradient. Senzaki, 2:33-62. It was well known in the prior art that ALD processes could be dialed-in to be self-limiting and that such processes have an "ALD window" in which the temperature of the substrate can be varied without changing the thickness of the film being deposited per ALD cycle. Min, for example, discloses an ALD process in which the deposition is self-limiting over a temperature range between 170°C and 210°C. Min, 8 & Fig. 3 (e.g., 40°C window). Thus, a POSA reading Senzaki's disclosure of an ALD process that varies the temperature to create a compositional gradient would have

understood from the teachings of Min that the temperature could be varied by 40°C and remain within the self-limiting ALD window.

86. A POSA also would have known that Senzaki's ALD process could create a compositional gradient by varying the flow rates of the metal precursor and the silicon precursor. 652 Patent (U.S. Pat. No. 6,042,652) at 3:42-4:25, 8:10-14. Dr. Gladfelter asserts that this is not disclosed in Senzaki because Senzaki discloses premixing the precursors. Ex.2120 (IPR2017-00664), ¶174. That the ALD precursors could be kept in different storage vessels, and not premixed, to deposit a multi-component film was obvious and well known in the prior art. *See* Buchanan, 20:25-49. Buchanan, for example, discloses using separate storage vessels for the Hf-containing precursor source mixture, the oxidant, and the Zr-containing precursor source mixture. Senzaki teaches using two precursors (Zr and Si alkylamide precursors) to achieve a compositional gradient. A POSA would have known to separately control the "flow" of each precursor. *See id.* at 19:42-53 (describing "flow"). It was standard to adjust the precursor flow rates and, in fact, it was standard to use different flow rates among the precursor gases in the ALD context. 652 Patent (U.S. Pat. No. 6,042,652), at 3:42-25, 8:10-14. Here, in an ALD context, Hyun describes using a lower flow rate for the oxygen gas, and "adjust[ing]" the flow rate. *Id.* Accordingly, it was well within the ordinary skill in the art (and in fact routine as part of ALD processes) to adjust the flow rate.

87. Dr. Gladfelter also argues that ALD with two different precursors may create issues with the precursors competing for surface sites. Ex.2120 (IPR2017-00664), ¶180. But this is precisely how the compositional gradient is achieved. More or less of a particular precursor reacts to achieve the compositional gradient.

C. A POSA Would Have Been Motivated To Combine Senzaki And Min

1. Senzaki And Min Do Not Have Inconsistent Goals Or Discourage A POSA From Combining Their Teachings

88. PO and Harvard argue that Senzaki and Min have inconsistent goals. POR at 35-40; Ex.2120 (IPR2017-00664), ¶¶182-89. I disagree. As an initial matter, Senzaki and Min both describe ALD at a single temperature and they both describe ALD by varying the temperature within a temperature range. As I described above, Senzaki discloses an ALD embodiment in which the temperature does not change. See Section VI.A. Senzaki also describes an ALD embodiment in which the temperature is varied to achieve a compositional gradient as discussed above. See Section VI.B. Min discloses an example of ALD at a single temperature. Min, 9 & Fig. 4 (e.g., self-limiting ALD at 200°C). Min also describes ALD in which the temperature is varied within an ALD window. *Id.* at 8-9 & Fig. 3. There, Min describes self-limiting ALD measured at five different temperatures between 170°C and 210°C. This 40°C temperature range in Min is consistent with Senzaki's temperature-varying embodiment, because Senzaki

recites a temperature change of at least 40°C. Senszaki, 2:50-53. This illustrates that Senszaki's teachings in regards to changing temperature to achieve a compositional gradient are fully consistent with self-limiting ALD, because the temperature can be changed within the ALD window (which is a temperature range).

89. Moreover, Senszaki and Min have a common goal. As I previously described, an express goal of Senszaki is to control the precise thickness of the gate dielectric layers, which is a goal that became particularly important as device sizes were shrinking in the late 1990s. Ex.1003 (IPR2017-00664), ¶133. As I previously explained, Min augments this goal by teaching self-limiting ALD, which precisely controls film thickness. *Id.* Accordingly, the references together support the common goal of precisely controlling the thickness of a film, such as a gate dielectric layer.

2. Dr. Gladfelter's Misreads The Senszaki/Min Combination

90. To be clear, my opinion that Senszaki, in view of Min invalidates claims 1, 2, 7, and 10 of the 016 Patent is based on Senszaki's ALD processes. My opinions are not based on modifying Senszaki's CVD recipes. Rather, my opinions are based on the obviousness of the claims based on Senszaki's ALD processes and, to the extent that Senszaki does not expressly describe "self-limiting" deposition,

dialing-in Senzaki's ALD processes to be self-limiting in view of Min's teaching.
See, e.g., Ex.1003 (IPR2017-00664), ¶114.

D. Senzaki In View Of Min And Shin Renders Obvious Claim 8

91. The Board noted in its decision that Patent Owner and Dr. Gladfelter do not "explain why the phase of a precursor at room temperature is relevant to whether that precursor will be useful in an ALD process." Decision at 13. In fact, it is not relevant, except to the extent that it affects the delivery method of the precursor. For example, the prior art describes different mechanical mechanisms (different ALD precursor delivery tools) for delivering precursors in different phases. Leskelä I, 19. None of these mechanisms is claimed in the 016 Patent.

92. Harvard and Dr. Gladfelter argue that CVD teachings do not always apply in the ALD context, and that contamination would deter a POSA from applying Shin's teaching to ALD. POR at 52-53. I disagree. Shin's CVD teachings provide a strong indication of suitability for ALD. It was well known that binary CVD reactions of the type described in Shin provide a strong indication that the same precursors would work in an ALD reaction. *See* Section III.A. And as I describe above, a POSA would not have had a contamination concern for ALD. *See* Section III.E.

93. Harvard and Dr. Gladfelter also argue that Shin's teaching would not have been predictable in the ALD context and not routine to implement. Petition at

54-57. First, as I describe in section III.A., binary CVD behavior provides a strong indication of ALD behavior. Moreover, metal dialkylamides were known to be suitable for ALD. Second, as I explain in Section III.B, dialing in a process into the ALD self-limiting window was routine. Accordingly, a POSA would have had a high expectation of success in using Shin's very similar precursor, and it would have been routine to dial-in the process in view of Min. *See also* Ex.1003 (IPR2017-00664), ¶¶141-45 (my initial declaration explaining motivations to combine).

94. Accordingly, as I described in my opening declaration, a POSA would have been motivated to use Shin's "comparable" compound, which would have been understood to "neutralize" the shortcomings of Senzaki's precursor and "incorporate[s] the advantages" of this claim of compounds. Ex.1003 (IPR2017-00664), ¶¶141-45.

VII. NO OBJECTIVE INDICIA SUPPORT THE NON-OBVIOUSNESS OF THE CLAIMS

95. I provided my opinions regarding objective indicia of non-obviousness in my opening declarations. *See* Ex.1003 (IPR2017-00662), ¶138; Ex.1003 (IPR2017-00663), ¶ 155; Ex.1003 (IPR2017-00664), ¶137. I understand, however, that PO and Dr. Gladfelter have raised additional details regarding purported objective indicia in the Patent Owner Responses and accompanying

declarations, and therefore I offer the additional opinions below to elaborate upon my opinions in the opening declarations and to rebut the new issues raised by PO and Dr. Gladfelter.

96. PO refers to "unexpected properties and results" of the claimed inventions, pointing to statements made by the named inventors themselves in the specifications of the 539 and 016 Patents. In my review of the specifications, however, I have seen no factual evidence from which a POSA could determine whether the claimed inventions actually displayed properties and results that were unexpected, relative to what was known in the art. The specification, for example, does not cite to any papers, patents, or textbooks that state what allegedly was "expected."

97. PO also refers to a "long-felt need" for depositing materials with high dielectric constants inside narrow trenches of semiconductor devices, citing a table in the 2000 International Technology Roadmap for Semiconductors ("ITRS") to support PO's claim that this problem allegedly would not be solved until at least 2008. In my opinion, this misinterprets the information in the ITRS. As shown in the chart cited by PO and Dr. Gladfelter, the ITRS *anticipated* that a new high- κ material would be needed for products that would ship in 2008. Ex.2108 (IPR2017-00662), at p. 1. As the table further shows, this *anticipated* problem did not exist for product shipments through at least 2005, because the enhancement of

dielectric constant, relative to the baseline of silicon dioxide, in those products was sufficiently provided using existing nitrided oxide techniques, which the chart abbreviates as "NO." *Id.* Thus, a POSA would have understood the ITRS to show that in the 2000 timeframe, there was no *existing* high- κ dielectric problem. Further, the ITRS merely shows that the high- κ dielectric requirement for advanced integrated circuits was expected to *arise* around 2008; it does not, contrary to PO's assertion, show that the problem would not be solved sooner.

98. PO and Dr. Gladfelter also allege that the claimed inventions experienced "great commercial success," pointing to sales figures for metal dialkylamide compounds that Dr. Gordon submitted in a declaration during prosecution of a related patent. I note that I addressed this assertion from the Gordon declaration in my opening declarations. See Ex.1003 (IPR2017-00662), ¶138; Ex.1003 (IPR2017-00663), ¶155; Ex.1003 (IPR2017-00664), ¶137. As I noted in my opening declarations, there is no evidence that these dialkylamide compounds were being used in ALD. Additionally, the challenged claims require more than just using a metal dialkylamide. The 539 Patent claims require using a metal dialkylamide precursor in ALD, with water or alcohol vapor, to deposit a metal oxide film. The 016 Patent claims require using a metal alkylamide precursor in self-limiting ALD with a second precursor, to deposit an insulator film that contains oxygen and the metal from the metal dialkylamide. There is no

evidence that the metal dialkylamides referenced by PO were being used for such processes.

99. PO also relies on a paper by Samsung and Genus, in which the authors of the paper thanked the named inventors for "helpful discussion on alkylamide precursors." Lee at p. 2. PO, however, claims that the authors "thanked Dr. Gordon for his teaching of the claimed inventions." See, e.g., Patent Owner Response (IPR2017-00662), at p. 48. As I noted in the previous paragraph, the "claimed inventions" of the challenged claims are not simply alkylamide precursors, many of which were known in the art decades before the 539 and 016 Patents were filed. In my opinion, it is therefore not correct to say that the authors of the Samsung/Genus paper "thanked Dr. Gordon for his teaching of the claimed inventions."

VIII. DECLARATION IN LIEU OF OATH

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

Reply Declaration to Patent Owner's Response to Petition for *Inter Partes* Review
of U.S. Patent Nos. 6,969,539 and 8,334,016 ("Banerjee Reply Decl.")

Dated: January 30, 2018



Sanjay Banerjee, Ph.D.