

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE PATENT TRIAL AND APPEAL BOARD

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MICRON TECHNOLOGY, INC.  
Petitioner

v.

PRESIDENT AND FELLOWS OF HARVARD COLLEGE  
Patent Owner

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

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

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

## **I. INTRODUCTION**

1. I repeat and reallege all the statements I made in my First Declaration, in paragraphs numbered 1 through 283, as though fully set forth herein.

2. I understand that grounds based on IPR2017-00663, Paper 1 (“’663 Petition), and IPR2017-00664, Paper 1 (“’664 Petition) remain at issue. 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, my discussion below will use the exhibit numbers from the ’663 Petition.

## **II. RELEVANT LEGAL STANDARDS**

3. My understanding of the legal standards for claim construction, anticipation, and obviousness in an *inter partes* review are as stated in my First Declaration, explained in paragraphs numbered 13 through 20, as incorporated herein by reference, *supra*.

## **III. ONE OF ORDINARY SKILL IN THE ART**

4. 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; *see also* e.g., ’663 Banerjee Decl. at ¶21.

5. I believe I am qualified based on my education and experience discussed above, to render opinions from the perspective of a POSA according to Petitioner’s proposed definition, and for the purpose of my opinions herein, I have used this definition. In particular, I have read the ’016 Patent, Buchanan, Senzaki, Min, Shin, the Deposition Transcript of Sanjay Banerjee, and have considered their disclosures from the perspective of such a POSA 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**

6. 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.

7. 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).

8. 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.

9. 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.

10. 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**

11. 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.*

12. 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**

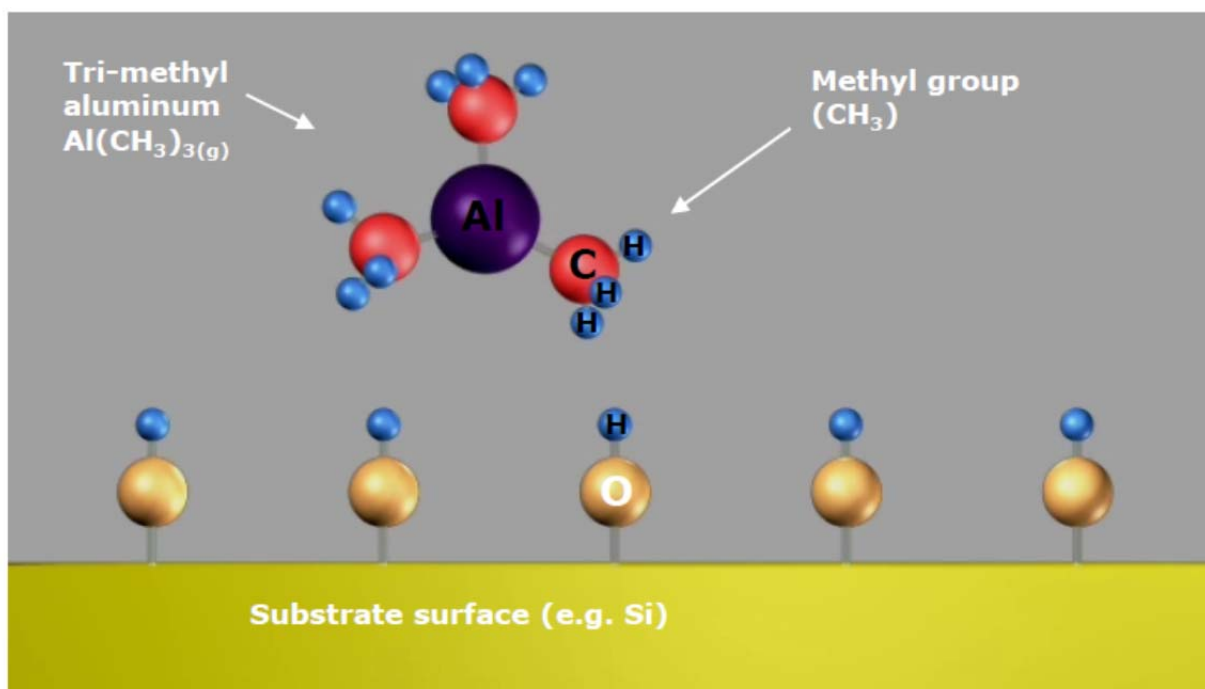
13. In an ALD deposition process, at least two reactant vapors are selected that will allow for the controlled, stepwise growth of a thin film on a heated surface. *See* Ex. 1013 at 13; Ex. 1001 at 20:56-21:8, 23:54-60, 24:8-15,

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.*

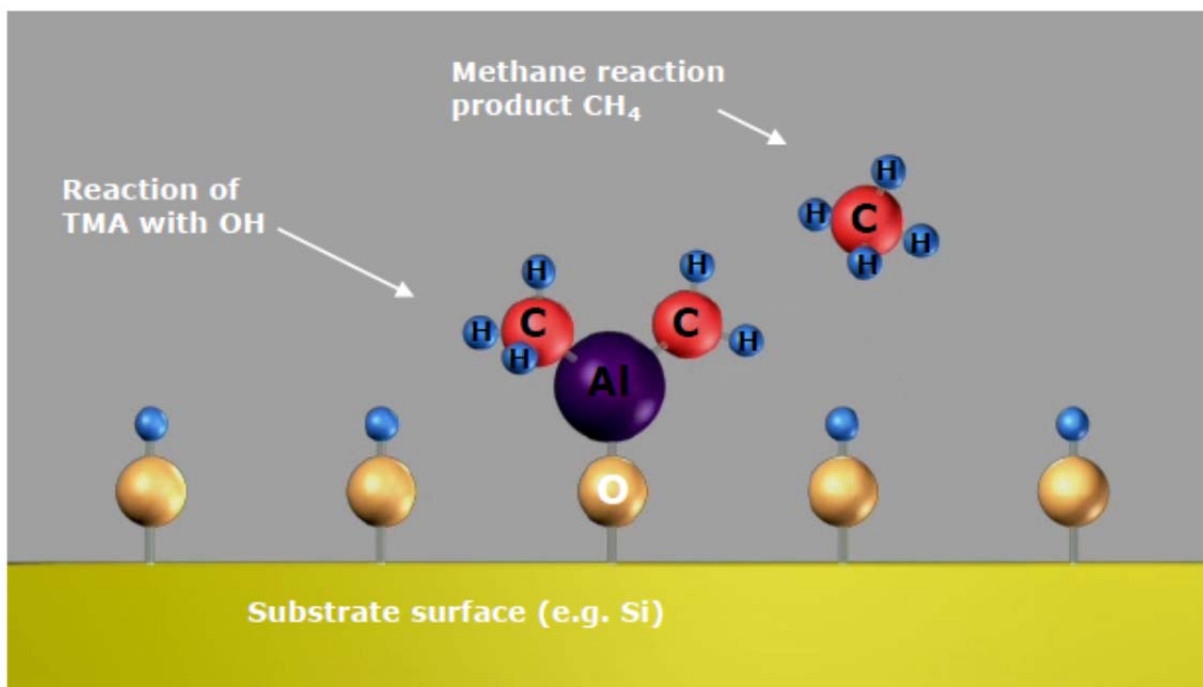
14. An advantage of ALD is that it can produce films having a uniform thickness over large areas even when the substrate surface exhibits features having

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.*

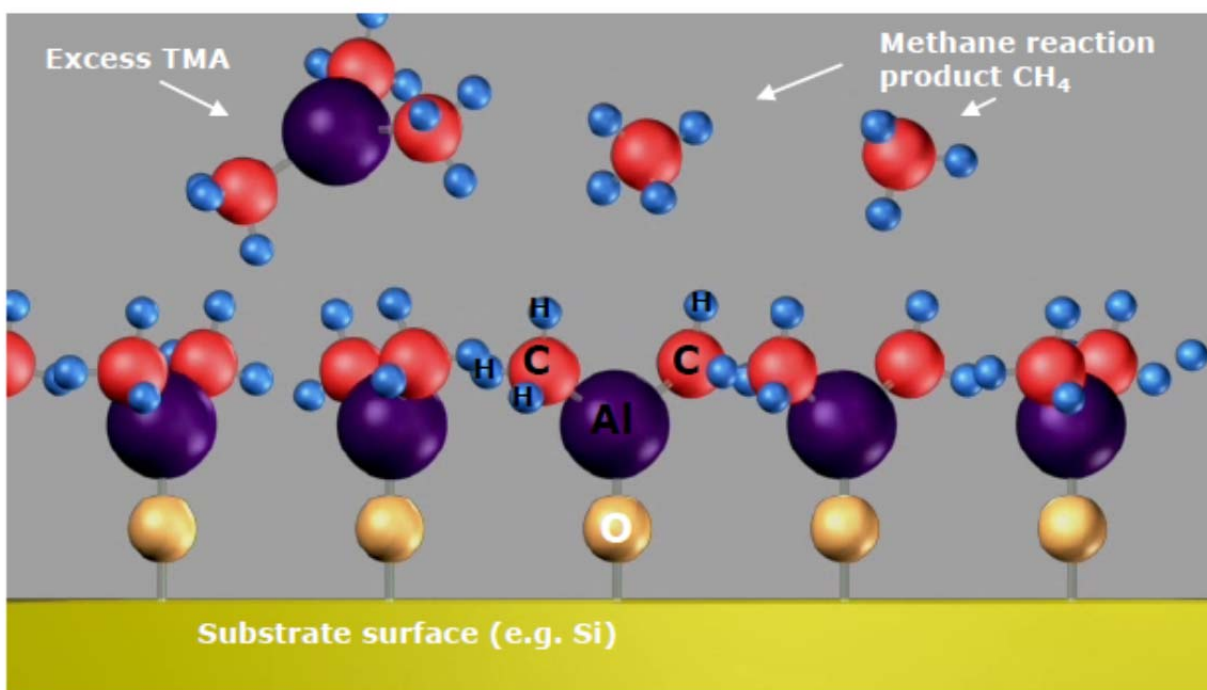
15. I often use demonstrative illustrations while teaching my students basic concepts, and similarly, I have found the following figures from a Stanford University ALD tutorial helpful in explaining the ALD deposition process. The figures in paragraphs 32-37 provide expanded views of the individual steps involved in the ALD of aluminum oxide thin films using trimethylaluminum,  $\text{Al}(\text{CH}_3)_3$  – abbreviated TMA, and water,  $\text{H}_2\text{O}$ , 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.



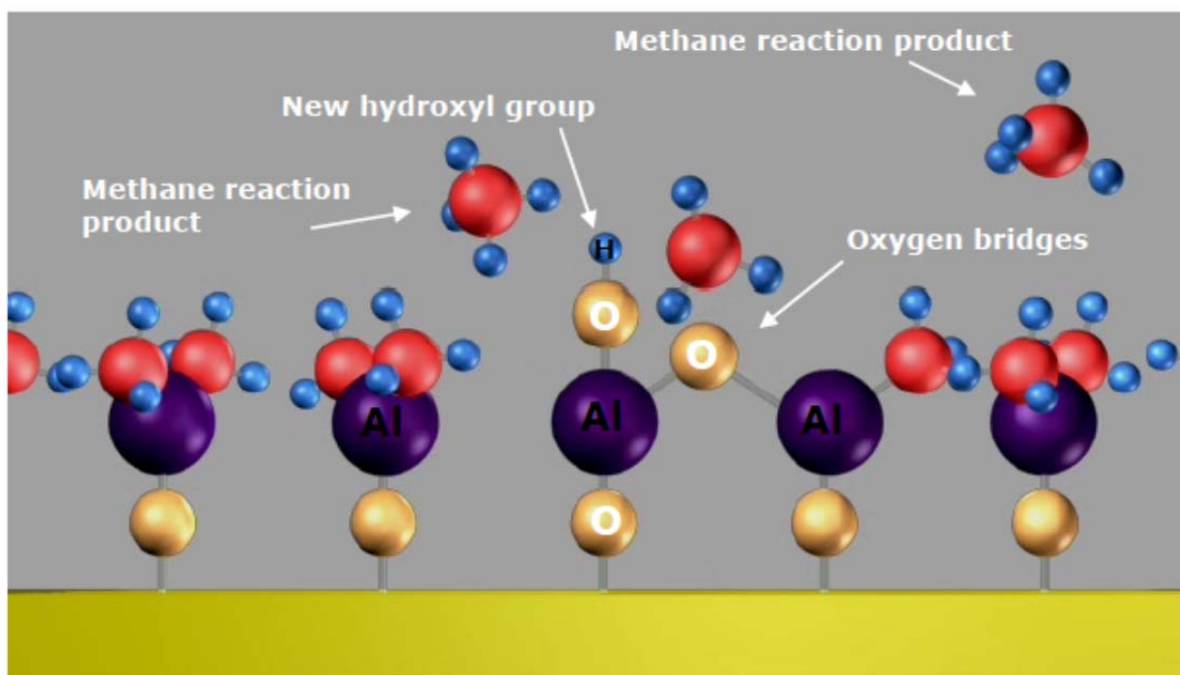
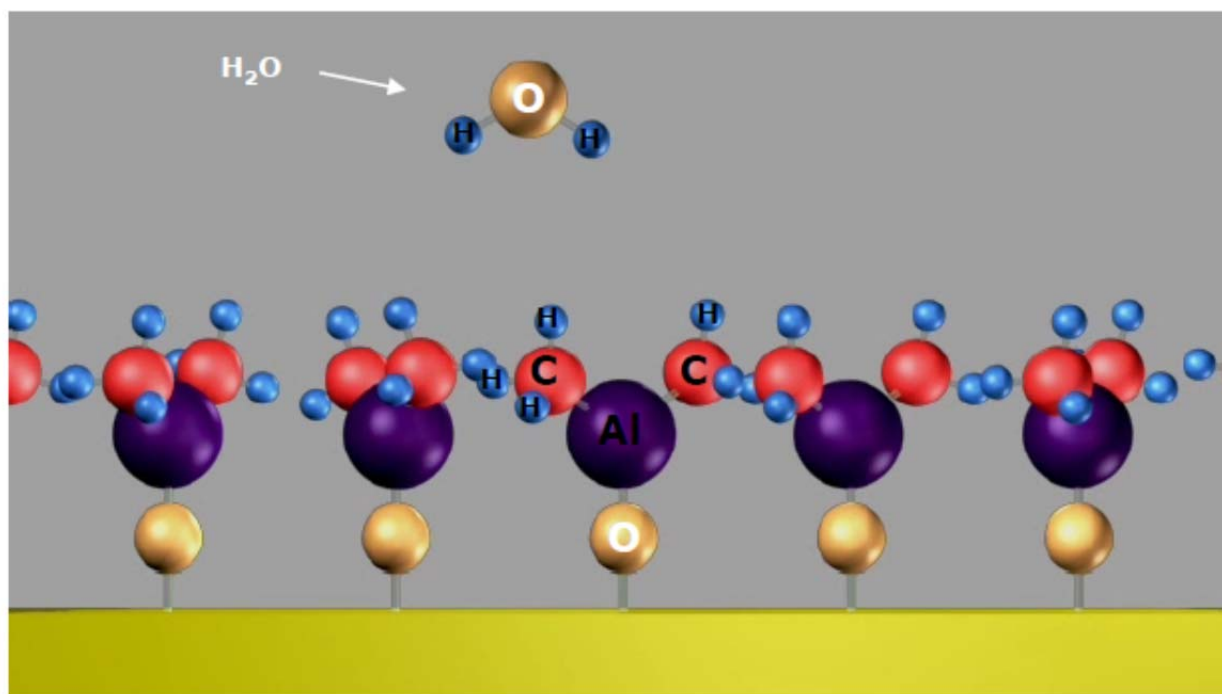
16. Reaction of TMA with a surface hydroxyl results in elimination of gaseous methane ( $\text{CH}_4$ ) and binding of the aluminum fragment to the surface. *Id.* at 5.



17. 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.

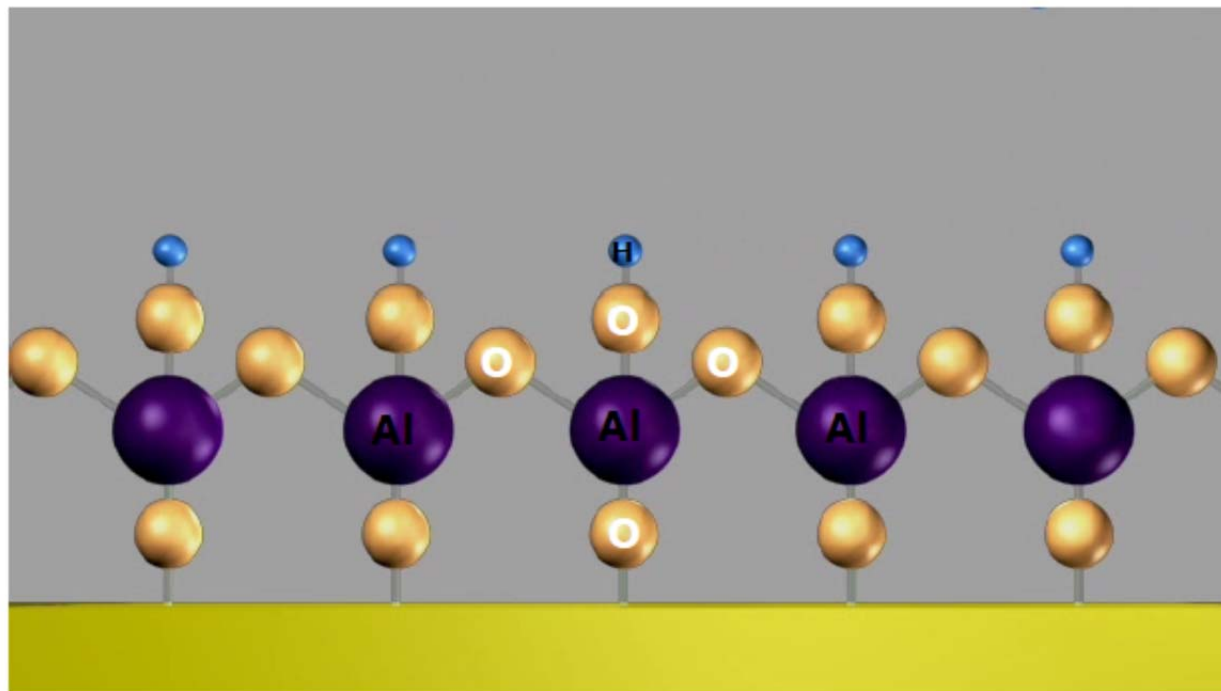


18. After the excess TMA is removed, water vapor, the second reactant component, is introduced into the reactor where it reacts with the methyl ( $\text{CH}_3$ ) groups attached to the aluminum. The reaction produces methane and leaves behind a hydroxyl group bound to the surface. Some of the surface hydroxyl groups will react with adjacent methyl groups to eliminate another methane and form an oxygen bridge between two aluminum atoms. *Id.* at 7.



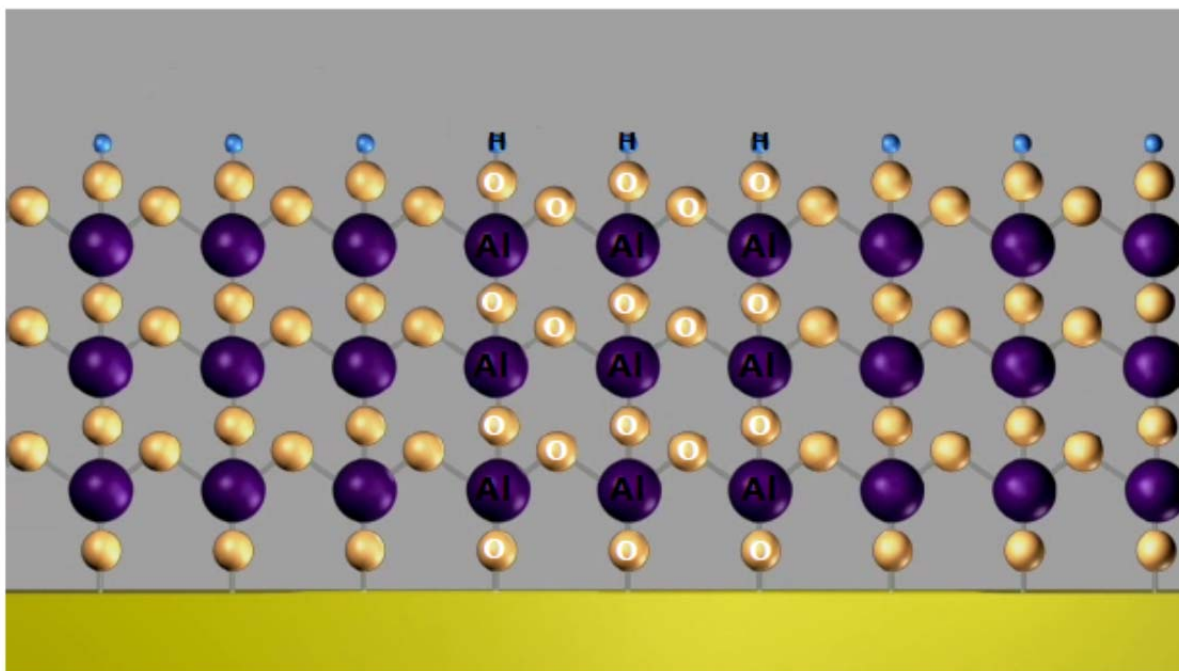
19. After all of the methyl groups have reacted with water, the surface is saturated with hydroxyl groups and excess water is swept from the reactor along

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.



20. 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.





21. 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.

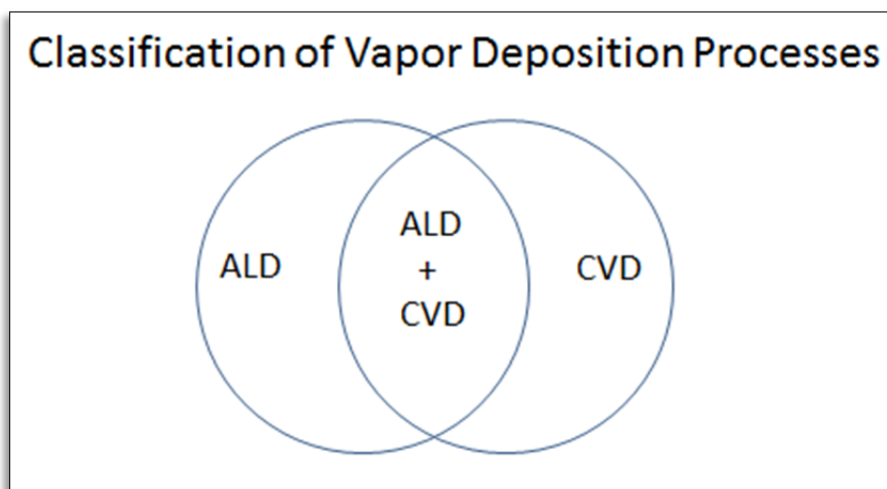
22. For example, the Petitions misleadingly state that ALD techniques were “well known” at the time of the inventions in the late 1990’s. *See, e.g.,* ’663 Petition at 7. However, it is more accurate to note that although ALD was developed in the seventies in Finland, by the late 90’s there were “a lot 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.*

23. 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.

24. 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.

25. 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.

26. Those of skill in the art further understood that precursor chemistry for CVD processes is also unpredictable, and that due to the significant differences between, and unpredictable nature of ALD and CVD processes, precursors that may be suitable for one process, are not necessarily suitable for the other. *See* Banerjee Tr. at 66:18-67:7 (“Yes, there can be some where CVD precursors may not work for ALD, that's correct.”), 74:15-23 (“Not all CVD precursors may work for ALD. . .”) 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* generally Ex. 2102, Jones.



27. The diagram above visually depicts how a POSA would have understood the relationship of precursors used in ALD and CVD processes. While there is overlap, not all precursors are suitable for both ALD and CVD. *See* Banerjee Tr. at 66:18-67:7, 74:15-23.

28. 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 at 6 (indicating that the films have Ti/N ratio close to 1 and contain significant carbon contamination); Ex. 2104, Ishihara at 4 (reporting deposition of CVD-TiN films from a  $\text{Ti}(\text{N}(\text{CH}_3)_2)_4\text{-NH}_3$  gas mixture and indicating that the films contained carbon impurity); Ex. 2105, Dubois '92 at 1 (reporting that thermal decomposition of  $\text{Ti}(\text{NMe}_2)_4$  on both  $\text{TiSi}_2$  and Al surfaces at temperatures up to 650 K yields films that contain titanium, nitrogen, and a significant amount of

carbon); Ex. 2106, Dubois '94 at 1<sup>1</sup> (reporting carbon contamination in TiN film produced via the reaction of tetrakis(dimethylamido) titanium and ammonia); Ex. 2114, Sugiyama at 5 (reporting carbon contamination in a variety of metal nitride films). 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

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<sup>1</sup> I note the in the '663 Institution Decision, the Board concluded the teachings of Dubois '94 are consistent with Min. Paper 11, at n.7. However, what is missing from the Board's analysis is that the referenced quotation from Dubois '94 refers to the gas phase infrared spectrum of TDMAT rather than the infrared spectrum of TDMAT bound to the surface. *See id.* (quoting Ex. 2106 at 1330 ("At temperatures below ~450 K the infrared spectrum is characteristic of the intact precursor.")). In the sentence immediately preceding the cited quote, Dubois writes "We have probed the source of carbon in the growth of titanium nitride thin films by following the pyrolysis of tdm<sub>2</sub>at *in the gas phase* using transmission infrared spectroscopy (see Fig. 1)..." Ex. 2106 at 1330 (emphasis added). A POSA would understand that reactions of precursors on surfaces will have a different temperature-dependent behavior than in the gas phase.

the resulting film are considered impurities in metal oxide films that should be avoided.

29. 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  $\text{HfO}_2$ , 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 have concluded that when the dialkylamido metal precursor is adsorbed onto the surface before the second reactant is added, its dialkylamido 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.

30. 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.

## **V. OPINION ON CLAIM CONSTRUCTION**

31. 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. OBJECTIVE INDICIA SHOW THAT CLAIMS 24, 26, AND 29 ARE NOT OBVIOUS**

32. The inventions are in an unpredictable, experimental field, meaning that even one skilled in the art cannot predict with a reasonable degree of certainty the outcome of an experiment regarding a class of precursors without actually performing it or a substantially similar one in a laboratory. Once the inventors tested the claimed methods and the class of compounds in the laboratory, they discovered that they possessed unexpectedly advantageous and superior properties, including liquid state at room temperature, higher decomposition temperature,

higher volatility, and other surprising results as reported by the inventors in the patent specification and elsewhere. Ex. 1001 at 19:55-20:7 (“surprisingly efficient,” “surprisingly fast,” and “surprisingly” successful at providing films over very high aspect ratios); *see also* Ex. 2133, Hausmann. Further, the use of the metal alkylamide precursors claimed in the challenged claims resulted in the deposition of metal oxide at unprecedented low temperatures and with the unexpected lack of detectable impurities such as carbon. *See, e.g.*, Ex. 1001 at 27:16-17; *see also* Ex. 2133. In addition to the demonstration of such unexpectedly superior properties, the inventions solved a long-felt need of the industry and have since achieved great commercial success. During the prosecution of the ’848 Patent, from which the ’016 Patent is a direct continuation, the patentee established the long-felt need and failure of others. *See*, Ex. 1021, Gordon Aug. 2008 Decl. The need to solve the problem of deposition of high dielectric materials inside narrow trenches for DRAM memory existed as early as the mid-1990s and was recognized by those of ordinary skill in the art. In fact, industry experts working on the 2000 International Technology Roadmap for Semiconductors did not expect a solution to this problem until *at least* 2008. Ex. 2108, ITRS.

33. In the late 1990s-2000s, there was a high degree of interest in investigating precursors for ALD processes to deposit high dielectric materials



inside of narrow trenches for DRAM. For example, a joint scientific paper written by Samsung Electronics and Genus Inc. (an ALD equipment supplier) confirms this point. *See* Ex. 2132, Lee. Samsung and Genus had many highly-skilled scientists and technologists working on, and failing to solve, the very problems that that the claimed invention solves. Despite such active efforts, this problem was not solved before the current invention was made by Dr. Gordon et al. In fact, the Samsung Paper specifically thanked Dr. Gordon for his teaching of the claimed inventions. *See* Ex. 2132 at 2 ( “The authors would like to thank Professor R. Gordon, D. Hausmann at Harvard University for helpful discussions on alkylamide precursors.”).

## VII. OPINIONS ON IPR2017-00663

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

34. Buchanan discloses tens of thousands of precursors without disclosing or rendering obvious that they are suitable for use in Example 3. Ex. 2116. A person of ordinary skill in the art (“POSA”) would know that precursor chemistry is unpredictable and would not have found it obvious to use Buchanan’s disclosed metal alkylamides in combination with Example 3, let alone in an ALD process to form a metal oxide film as recited by the Challenged Claims.

**B. Buchanan Does Not Disclose That All Its Precursors Are Suitable For Both CVD And ALD**

35. Buchanan provides, as a general disclosure, a large number of precursors that can potentially be used to form a precursor source mixture. *See* Buchanan at 4:1-21; 5:22-37. Buchanan enumerates that the group of potential “precursors” includes,

any compound which contains 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 (H), alkyl (CR<sub>3</sub>), alkenyl (CR<sub>2</sub>CR<sub>2</sub>), cycloalkenyl, aryl, alkyne (CCR), carbonyl (CO), amido (NR<sub>2</sub>), imido (NR), hydrazido (NRNR<sub>2</sub>), phosphido (PR<sub>2</sub>), nitrosyl (NO), nitryl (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), nitrile (RCN), isonitrile (RNC), halide (F, Cl, Br, or I), azide (N<sub>3</sub>), alkoxy (OR), siloxy (OSiR<sub>3</sub>) silyl (SiR<sub>3</sub>), and halogenated, sulfonated or silyated derivatives thereof and when delivered to a vaporizer the precursor is readily converted into gaseous form.

Buchanan at 5:22-37.

Buchanan further provides that,

[a] generalized formula for the precursor of the present invention is



where M is 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; R<sub>1</sub> and R<sub>2</sub> are the same or different ligands 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 silyated derivatives thereof; A is an optional coordinatively bound or associated ligand selected from the group consisting of phosphines (R<sub>3</sub>P), phosphites ((RO)<sub>3</sub>P), amines (R<sub>3</sub>N), arsines (R<sub>3</sub>As), stibenes (R<sub>3</sub>Sb), ethers (R<sub>2</sub>O), sulfides (R<sub>2</sub>S), nitriles (RCN), isonitriles (RNC) alkenes, hydrazine, pyridines, nitrogen heterocycles, macrocycles, schiff bases, cycloalkenes, alcohols (ROH), phosphine oxides (R<sub>3</sub>PO), alkylidenes, nitrites, alkynes, and water;  $x \geq 1$ ;  $x+y =$  the valence of the element M;  $y \geq 0$ ; and z is  $\leq 0$ .

Buchanan at 5:44-65.

36. Therefore, the set of all potential precursors that Buchanan discloses includes at least tens of thousands of possible combinations. Buchanan goes on to identify that (M) may be one of fifty (50) metal elements and ( $R^1_x$  and  $R^2_y$ ) may each be one of at least twenty (20) classes of ligands. A POSA would further know that each ligand includes many different permutations resulting in exponentially more possible choices for ( $R^1_x$  and  $R^2_y$ ).

37. I understand that the Petitioner alleges that Buchanan discloses that each and every one of these precursors can be used in any CVD or ALD process and consistently refers to the language in Buchanan below in support of its allegation:

*The precursor source mixture of the present invention can be used in any CVD or ALD process* with any delivery means currently employed. Thus, the invention is not limited to a specific CVD or ALD apparatus or to any delivery system. . . .

In accordance with the present invention, a film is formed on a substrate *utilizing the precursor source mixture* of the present invention in any CVD or ALD process.

Buchanan at 7:30-43 (emphasis added); see Petition at 23, 34-35 (citing Buchanan at 7:30-32, 7:41-43); *id.* at 39, 46, 47 (citing Buchanan at 7:30-32).

38. In my opinion, a POSA would not have interpreted Buchanan, as Petitioner has alleged, to be directed primarily at disclosing a set of precursors. Rather, a POSA would have understood that Buchanan is primarily directed to the use of an inert organic liquid as a solvent to form a precursor source mixture for delivery to a CVD or ALD reactor. *See* Buchanan at Abstract, 3:56-4:21, 29:14-34:30. A POSA would have understood that Buchanan's list of precursors and the language referenced above was meant to provide that Buchanan's *precursor source mixture* is not limited to a single class of metals or ligands or to a particular CVD or ALD delivery system. In other words, a POSA would have understood that Buchanan discloses a multitude of precursors merely to indicate that the disclosed delivery method, which uses an inert organic liquid, has wide applicability, not to indicate that each disclosed precursor is suitable for use in a CVD or an ALD process.

39. A POSA would not have understood Buchanan to disclose that each and every one of the tens of thousands of disclosed precursors can be used in any CVD or ALD process. In particular, a POSA would not interpret Buchanan's list of precursors or disclosure that "[t]he precursor source mixture of the present invention can be used in any CVD or ALD process with any delivery means currently employed" to literally mean that any precursor, of the tens of thousands of disclosed precursors, can be used with any CVD or ALD process. Instead, a

POSA would have recognized that Petitioner's interpretation of Buchanan to be inconsistent with the state of the art and untenable on its face.

40. A POSA would have immediately understood that not every precursor disclosed in Buchanan can be used for both CVD and ALD. *See* Banerjee Tr. at 66:18-67:7, 74:15-23.

41. A POSA would have understood that the chemistry involved in the formation of a metal film via an ALD process is unpredictable, and while pre-process calculations are useful, testing would be required to determine whether a given precursor could be used in an ALD reaction to form a desired film. *See, e.g.,* Banerjee Tr. at 89:14-90:26; Ex. 1008 at 20; Ex. 1046 at 8.

42. Petitioner's own expert, Dr. Banerjee supports this understanding. *See* Banerjee Tr. at 73:15-74:6; 89:14-2. Dr. Banerjee testified that to determine whether a particular precursor disclosed in Buchanan could work in ALD a POSA would first look up "in standard handbooks" or "other sources" the chemical bond strengths of the precursors. *See* Banerjee Tr. at 73:15-74:6. The chemical bond strengths "would give a person of ordinary skill a very good start in terms of choosing a precursor for a particular ALD process." Banerjee Tr. at 74:3-6 (emphasis added). But the information regarding the bond strengths is not sufficient to determine whether a precursor would be suitable for use in an ALD process. *See* Banerjee Tr. at 89:14-90:2. Rather, as Dr. Banerjee further testified,

the information in handbooks or other sources “should give a person of ordinary skill strong hints as to which precursors might be suitable for ALD . . . . But of course, you know, chemistry is a science and at the end of the day, you do want to do experiments to make sure that what a strong suggestions based on thermodynamics are borne out in the lab.” Banerjee Tr. at 89:14-90:2.

43. Therefore, in considering whether one of Buchanan’s disclosed precursors can be used in Buchanan’s Example 3, or any particular ALD process, a POSA would first have to consider additional references and then would have to test the precursor to determine its suitability.

44. As a result, a POSA would have known one could not assume that each and every precursor in Buchanan’s list of tens of thousands of precursors is suitable for CVD or ALD. A POSA considering Buchanan’s disclosed precursors would not know which precursors could be used in a CVD or an ALD process without seeking more information.

45. As discussed in more detail below, a POSA considering Buchanan’s disclosed precursors would have found that not all of the disclosed precursors, including precursors identified as “preferred” and “highly preferred,” are suitable for use in CVD or ALD processes as Petitioner alleges. For example, a POSA would understand that many of these possible precursors are not known to exist, and to the extent they may exist, they cannot be stably synthesized and isolated,

which obviously makes performing CVD and ALD with these chemicals impossible.

**C. Not All Precursors Disclosed In Buchanan Are Suitable For Both CVD And ALD**

46. With respect to ALD processes, Petitioner's expert, Dr. Banerjee, testified that "to design an ALD process, you have to choose a precursor and the ALD deposition conditions []." Banerjee Tr. at 74:12-14. A POSA would know that in order for a precursor to be suitable for ALD, it must meet several criterion. First, a precursor must exist in a stable, synthesizable form. Second, if the precursor is a solid or liquid, it must have sufficient volatility to allow the vapor to be transported into the ALD or CVD deposition chamber. Third, if a potential precursor can be synthesized and has sufficient stability, one would understand that it must also possess several additional properties: 1) the precursor must have sufficient volatility to allow the vapor to be transported into the ALD; 2) the precursor should exhibit thermal stability at the substrate temperatures; 3) the precursor must be able to chemisorb on or react with the surface; 4) the adsorbed first precursor must react with the second precursor aggressively; 5) side-products in the reaction must be gaseous; 6) precursors should not cause etching of the deposited film; 7) the precursor should not dissolve in the film; and 8) the



precursor must be compatible with the underlying substrate. *See* Ex. 1013 at 13-14.

47. A POSA would have known that not all precursor complexes meet all of these conditions. Further, a POSA would have recognized, therefore, that any broad, systematic, and formulaic disclosure of potential precursors, such as the disclosure in Buchanan, is likely to contain many precursors that are not suitable for ALD as well as some that are.

48. Regarding the first requirement, that a precursor must be able to be synthesized in a sufficiently stable form to be suitable for use in a CVD or an ALD process, Buchanan discloses a number of potential precursors for which there appears to be no indication in chemical literature that they have been synthesized or they can only be synthesized under such extreme conditions, e.g., via trapping in low-temperature matrices, that render them unsuitable for use in a CVD or an ALD process. This includes not only chemicals that are disclosed through Buchanan's general formula but also several of the "preferred" and "highly preferred" precursors that Buchanan enumerates specifically. *See* Buchanan at 8:45-18:34 (Precursor Source Mixtures for Hydride, Alkyl, Alkenyl, Carbonyl, Alkoxy, Amino, Phosphido, Nitrate, Halide, and Silyl-Containing Compounds).

49. In addition to precursors that are not known to stably exist, Buchanan discloses precursors that are not compatible with CVD and/or ALD because they

fail to satisfy at least one of the other requirements enumerated above. For example, Buchanan discloses precursors that are not thermally stable at the required substrate temperatures, and precursors that do not chemisorb on or react with the substrate surface. A POSA would know that “when you talk about CVD or ALD processes, you cannot divorce the molecule from the deposition conditions.” Banerjee Tr. at 65:11-15. While these precursors may exist, they cannot be used with the process conditions necessary for CVD and/or ALD processes.

**1. Buchanan Discloses Compounds That Cannot Be Stably Synthesized and Isolated**

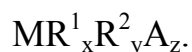
50. Although it should go without saying that a CVD or ALD precursor must exist, Buchanan identifies many precursors that appear not to exist. More precisely, Buchanan discloses several precursors, including Buchanan’s “preferred” and “highly preferred” precursors, that appear to have never been stably synthesized or isolated, based on their absence in the chemical literature. In some such cases one would not expect to be able to synthesize them.

51. A POSA would understand that, regardless of whether the precursor is a gas, liquid, or solid, it must be sufficiently stable to allow storage in suitable delivery vessels. This excludes the use of compounds prepared under highly specialized conditions such as found in a low-temperature matrix or compounds

that may have been postulated to exist for fleeting moments as an intermediate in a chemical reaction.

52. Buchanan discloses a number of precursors that do not meet this basic criterion. In particular, for some of the compounds, including Buchanan's "preferred" precursor, tetrakis(trifluorophosphine)Iridium ( $\text{Ir}(\text{PF}_3)_4$ ), I was not able to find any report of synthesis. For other compounds such as bis(benzene)-cobalt ( $\text{Co}(\text{C}_6\text{H}_6)_2$ ), synthesis may be possible through specialized techniques, such as low-temperature matrix isolation; however, as discussed more fully below, the resulting compound is unstable above  $-3^\circ\text{C}$  and cannot be isolated and used as a precursor. *See* Ex. 2110, Bechamp at 4, 5, 8.

53. As discussed above, Buchanan discloses that a generalized formula for the precursor of the present invention is:



Buchanan at 5:44–46.

54. In my opinion I could use Buchanan's general formula to identify a great number of compounds that fit this formula but cannot be stably synthesized. Further, Buchanan's disclosure of precursors that cannot be stably synthesized and isolated is not limited to those made possible by Buchanan's generalized formula. Buchanan also discloses several precursors designated as being "preferred" or "highly preferred" that are unknown or are not stable enough to serve as a

precursor. I will explain several illustrative examples of all these categories below, but this should not be construed as exhaustive or limiting.

**a. Buchanan Discloses The Use Of Precursors Containing Francium, Which Cannot Be Stably Synthesized**

55. Buchanan's list of disclosed precursors includes francium (Fr).

Buchanan 5:48-51.

where M is 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; R<sup>1</sup> and R<sup>2</sup> are the same or different ligands

Buchanan 5:48-51 (annotated).

56. A POSA would know that Francium (Fr) cannot be used as a CVD or ALD precursor because Francium (Fr) is a radioactive element whose longest-lived isotope has a 22-minute half-life.

57. Samples of pure francium could not be identified to exist in the chemical literature. Therefore, in my opinion, precursor complexes containing Francium cannot be used as a precursor for ALD or CVD because they cannot be stably synthesized or stored.

**b. Buchanan Discloses The Use Of Metal Carbonyl Precursors That Are Unknown To Exist**

58. Buchanan discloses the use of metal carbonyl precursors. For example, as shown below, Buchanan's generalized formula discloses precursors in

which the metal (M) is aluminum (Al), gallium (Ga), indium (In) or thallium (Tl),  $R^1_x$  is the carbonyl ligand (CO), and  $R^2_y$  is the halide ligand fluoride, chloride, bromide or iodide. Buchanan 5:48-55.

where M is 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;  $R^1$  and  $R^2$  are the same or different ligands 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

Buchanan 5:48-55 (annotated).

59. None of these precursors could be found in the chemical literature to exist in a sufficiently stable form to be suitable for use in a CVD or an ALD process. While many examples of metal carbonyls exist among the so-called transition elements (those belonging to Groups 3 to 10 in the periodic table of elements), it is uncommon among the main group elements (Groups 1, 2, 11-18). In general, stability of carbonyl ligands occurs when the metal element has valence electrons in suitable orbitals available for so-called “back-bonding” with CO. The main group elements, Al, Ga, In and Tl do not have electrons in suitable orbitals for “back-bonding.”

60. Therefore, in my opinion, Metal Carbonyl Precursors of Al, Ga, In, and Tl cannot be used as a precursor for ALD or CVD because they cannot be stably synthesized.

c. **Buchanan Specifically Discloses The Use Of Tetrakis(Trifluorophosphine)Iridium, Which Is Unstable**

61. Buchanan specifically discloses that tetrakis(trifluorophosphine)iridium ( $\text{Ir}(\text{PF}_3)_4$ ) is a “preferred precursor.”

preferred precursors are dimethyl-, diethyl-, or diisobutyl-B, Al, Ga, In, As, or Sb hydride;  $\text{Me}_2\text{AlH}(\text{NEtMe}_2)$ ; tertbutylarsine;  $(\text{Me}_3\text{N})\text{AlH}_3$ ;  $(\text{EtMe}_2\text{N})\text{AlH}_3$ ;  $(\text{Et}_3\text{N})\text{AlH}_3$ ;  $\text{CpWH}_2$ ;  $\text{Cp}_2\text{MoH}_2$ ; trimethyl-, triethyl-, triisobutyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or eth-  
...  
15 pentyl) $_4\text{Cr}$ ;  $\text{Et}_3\text{Pb}(\text{neopentoxy})$ ;  $\text{Cp}_2\text{Me}_2\text{Zr}$ ;  $(\text{MeNC})_2\text{PtMe}_2$ ;  $\text{CpIr}(\text{C}_2\text{H}_4)_2$ ; bis Cp-Co, Mo, Fe, Mn, Ni, Ru, V, Os, Mg or Cr; bisethylbenzene-, bisbenzene-Co, Mo or Cr; triphenyl-Bi, Sb, or As; trivinylboron; trisCp-Sc, Y, La, Ce,  
...  
tatriene) Mo  $(\text{CO})_3$ ;  $\text{NdCp}_3$ ;  $\text{SmCp}_3$ ;  $\text{ScCp}_3$ ;  $\text{TbCp}_3$ ;  $\text{TiCp}$ ;  
25  $\text{TmCp}_3$ ;  $\text{Cp}_2\text{WH}_2$ ; (mesitylene) $\text{W}(\text{CO})_3$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}(\text{CO})_2$ ;  $\text{Ir}(\text{allyl})_3$ ;  $\text{Pt}(\text{allyl})_2$ ;  $\text{CpIr}(\text{cyclooctanedione})$ ;  $[\text{Ir}(\text{OMe})(\text{cyclooctanedione})]_2$ ;  $\text{Ru}(\text{cyclooctanedione})(\text{allyl})_2$ ;  $\text{Ru}_3\text{CO}_{12}$ ;  $\text{Fe}(\text{CO})_5$ ;  $\text{CO}_2(\text{CO})_8$ ;  $\text{Ru}(\text{CO})_3$  (1,3-cyclohexadiene);  $\text{Os}_3\text{CO}_{12}$ ;  $\text{Cr}(\text{CO})_6$ ;  $\text{CpCO}(\text{CO})_2$ ;  $\text{Mn}_2(\text{CO})_{10}$ ;  $\text{CpMn}(\text{CO})_3$ ;  $\text{Mo}(\text{CO})_6$ ;  $\text{Ni}(\text{CO})_4$ ;  $\text{Re}_2(\text{CO})_{10}$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}(\text{CO})_2$ ;  $\text{Ru}_3(\text{CO})_{12}$ ;  $\text{W}(\text{CO})_6$ ;  $\text{CpV}(\text{CO})_4$ ;  $\text{CF}_3\text{CO}(\text{CO})_4$ ;  $\text{Pt}(\text{CO})_2(\text{cyclooctanedione})$ ;  $\text{Ir}(\text{CO})_2(\text{cyclooctanedione})$ ;  $(\text{CO})_4\text{Fe}[\text{P}(\text{OCH}_3)_3]$ ;  $(\text{CO})_4\text{Fe}[\text{N}(\text{CH}_3)_3]$ ;  $\text{CoNO}(\text{CO})_3$ ; butoxy,  $\text{OCH}(\text{CF}_3)_2$ ,  $\text{OCMe}_2(\text{CF}_3)$ ,  $\text{OCMe}(\text{CF}_3)_2$ ,  $\text{OSi}$   
...  
tbutoxy) $\text{CuPMe}_3$ ;  $\text{Pt}(\text{PF}_3)_4$ ;  $\text{Ni}(\text{PF}_3)_4$ ;  $\text{Cr}(\text{PF}_3)_6$ ;  $(\text{Et}_3\text{P})_3\text{Mo}(\text{CO})_3$ ;  $\text{Ir}(\text{PF}_3)_4$ ;  $\text{Ti}(\text{NO}_3)_4$ ;  $\text{Zr}(\text{NO}_3)_4$ ;  $\text{Hf}(\text{NO}_3)_4$ ;  $\text{Si}(\text{CH}_3)_3(\text{NO}_3)$ ;  $\text{RuNO}(\text{NO}_3)_3$ ; gallium nitrate;  $\text{Sn}(\text{NO}_3)_4$ ;  $\text{Co}(\text{NO}_3)_3$ ;  
60  $\text{VO}(\text{NO}_3)_3$ ;  $\text{CrO}_2(\text{NO}_3)_2$ ;  $\text{TiCl}_4$ ;  $\text{HfCl}_4$ ;  $\text{ZrCl}_4$ ;  $\text{InCl}_2$ ;  $\text{ZnCl}_2$ ;

Buchanan at 6:1-61 (emphasis added).

62. Trifluorophine ( $\text{PF}_3$ ) is known to form metal complexes that have properties that parallel those of metal carbonyls (metal complexes with carbon monoxide (CO) ligands). The anion  $[\text{Ir}(\text{PF}_3)_4]^-$  is known; however, due to its ionic nature, a POSA would understand that it is not volatile and, therefore, that it is not useful as a precursor in ALD. The neutral compound, which is identified in Buchanan at 6:59, is unknown in the chemical literature in an isolated state.

63. To the extent that the neutral compound,  $\text{Ir}(\text{PF}_3)_4$ , can be isolated, a POSA would not expect it to be stable. A simple, but powerful, guideline for understanding stability of low valent, transition metal complexes, such as  $\text{Ir}(\text{PF}_3)_4$ , is the 18-electron rule. This rule, which is based upon bonding considerations taught in elementary inorganic or organometallic chemistry courses, states that the most stable formula for a complex is the one in which the total number of valence electrons from the metal are combined with the electrons contributed by the ligands equals 18. *See generally* Ex. 2118, Green; *see also id.* at 2-3 (“The large majority of the transition metal complexes with metal-carbon organic, -carbonyl or -hydride ligands isolable at room temperature can be regarded as having 18 electrons in their valence shell. This is the empirical basis of the rule ‘a valence shell containing 18 electrons gives stable complexes’.”) (emphasis added). In  $\text{Ir}(\text{PF}_3)_4$ , each  $\text{PF}_3$  ligand contributes two electrons and the iridium contributes 9

leading to a total 17 electrons. As a result one would not expect  $\text{Ir}(\text{PF}_3)_4$  to be stable enough to serve as a precursor.

64. Therefore, in my opinion,  $\text{Ir}(\text{PF}_3)_4$ , cannot be used as a precursor for ALD or CVD because it cannot be stably synthesized or isolated.

**d. Buchanan Specifically Discloses The Use Of Cyclooctanedione Complexes, Which Are Unstable**

65. Buchanan specifically discloses several cyclooctanedione complexes,  $\text{CpIr}(\text{cyclooctanedione})$ ,  $\text{Ir}(\text{CO})_2(\text{cyclooctanedione})$ ,  $[\text{Ir}(\text{OMe})(\text{cyclooctanedione})]_2$ ,  $\text{Ru}(\text{cyclooctanedione})(\text{allyl})_2$ , and  $\text{Pt}(\text{CO})_2(\text{cyclooctanedione})$ , which Buchanan identifies as “preferred precursors”.



preferred precursors are dimethyl-, diethyl-, or diisobutyl-B,  
 Al, Ga, In, As, or Sb hydride;  $\text{Me}_2\text{AlH}(\text{NEtMe}_2)$ ; tertbutyl-  
 arsine;  $(\text{Me}_3\text{N})\text{AlH}_3$ ;  $(\text{EtMe}_2\text{N})\text{AlH}_3$ ;  $(\text{Et}_3\text{N})\text{AlH}_3$ ;  
 $\text{CpWH}_2$ ;  $\text{Cp}_2\text{MoH}_2$ ; trimethyl-, triethyl-, triisobutyl-, tri-n-  
 5 propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or eth-  
 . . . .  
 15 pentyl) $_4\text{Cr}$ ;  $\text{Et}_3\text{Pb}(\text{neopentoxy})$ ;  $\text{Cp}_2\text{Me}_2\text{Zr}$ ;  $(\text{MeNC})_2$   
 $\text{PtMe}_2$ ;  $\text{CpIr}(\text{C}_2\text{H}_4)_2$ ; bis Cp-Co, Mo, Fe, Mn, Ni, Ru, V, Os,  
 Mg or Cr; bisethylbenzene-, bisbenzene-Co, Mo or Cr;  
 triphenyl-Bi, Sb, or As; trivinylboron; trisCp-Sc, Y, La, Ce,  
 . . . .  
 tatriene) Mo  $(\text{CO})_3$ ;  $\text{NdCp}_3$ ;  $\text{SmCp}_3$ ;  $\text{ScCp}_3$ ;  $\text{TbCp}_3$ ;  $\text{TlCp}$ ;  
 25  $\text{TmCp}_3$ ;  $\text{Cp}_2\text{WH}_2$ ; (mesitylene) $\text{W}(\text{CO})_3$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}$   
 $(\text{CO})_2$ ;  $\text{Ir}(\text{allyl})_3$ ;  $\text{Pt}(\text{allyl})_2$ ;  $\text{CpIr}(\text{cyclooctanedione})$ ;  $[\text{Ir}$   
 $(\text{OMe})(\text{cyclooctanedione})]_2$ ;  $\text{Ru}(\text{cyclooctanedione})(\text{allyl})_2$ ;  
 $\text{Ru}_3\text{CO}_{12}$ ;  $\text{Fe}(\text{CO})_5$ ;  $\text{CO}_2(\text{CO})_8$ ;  $\text{Ru}(\text{CO})_3$  (1,3-cyclohexadi-  
 ene);  $\text{Os}_3\text{CO}_{12}$ ;  $\text{Cr}(\text{CO})_6$ ;  $\text{CpCO}(\text{CO})_2$ ;  $\text{Mn}_2(\text{CO})_{10}$ ;  $\text{CpMn}$   
 30  $(\text{CO})_3$ ;  $\text{Mo}(\text{CO})_6$ ;  $\text{Ni}(\text{CO})_4$ ;  $\text{Re}_2(\text{CO})_{10}$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}$   
 $(\text{CO})_2$ ;  $\text{Ru}_3(\text{CO})_{12}$ ;  $\text{W}(\text{CO})_6$ ;  $\text{CpV}(\text{CO})_4$ ;  $\text{CF}_3\text{CO}(\text{CO})_4$ ;  
 $\text{Pt}(\text{CO})_2(\text{cyclooctanedione})$ ;  $\text{Ir}(\text{CO})_2(\text{cyclooctanedione})$ ;  
 $(\text{CO})_4\text{Fe}[\text{P}(\text{OCH}_3)_3]$ ;  $(\text{CO})_4\text{Fe}[\text{N}(\text{CH}_3)_3]$ ;  $\text{CoNO}(\text{CO})_3$ ;  
 butoxy,  $\text{OCH}(\text{CF}_3)_2$ ,  $\text{OCMe}_2(\text{CF}_3)$ ,  $\text{OCMe}(\text{CF}_3)_2$ ,  $\text{OSi}$   
 . . . .  
 tbutoxy) $\text{CuPMe}_3$ ;  $\text{Pt}(\text{PF}_3)_4$ ;  $\text{Ni}(\text{PF}_3)_4$ ;  $\text{Cr}(\text{PF}_3)_6$ ;  $(\text{Et}_3\text{P})_3\text{Mo}$   
 $(\text{CO})_3$ ;  $\text{Ir}(\text{PF}_3)_4$ ;  $\text{Ti}(\text{NO}_3)_4$ ;  $\text{Zr}(\text{NO}_3)_4$ ;  $\text{Hf}(\text{NO}_3)_4$ ;  $\text{Si}(\text{CH}_3)_3$   
 60  $(\text{NO}_3)$ ;  $\text{RuNO}(\text{NO}_3)_3$ ; gallium nitrate;  $\text{Sn}(\text{NO}_3)_4$ ;  $\text{Co}(\text{NO}_3)_3$ ;  
 $\text{VO}(\text{NO}_3)_3$ ;  $\text{CrO}_2(\text{NO}_3)_2$ ;  $\text{TiCl}_4$ ;  $\text{HfCl}_4$ ;  $\text{ZrCl}_4$ ;  $\text{InCl}_2$ ;  $\text{ZnCl}_2$ ;

Buchanan at 6:1-61 (emphasis added).

66. Cyclooctanedione is an organic compound that has four isomeric forms - none of which is specified in the formulas cited in the patent. Regardless, none of these compounds are known to exist based on their absence from literature as searched by Chemical Abstracts. I could envision that one might be able to synthesize some of these compounds for specific cyclooctanedione isomers, but it is difficult to predict their stability and their volatility.

67. None of these precursors could be located in the chemical literature to be stably synthesized and isolated.

68. Therefore, in my opinion, cyclooctanedione complexes cannot be used as a precursor for ALD or CVD because they cannot be stably synthesized or isolated.

e. **Buchanan Specifically Discloses The Use Of Bis(Benzene)Cobalt, Which Is Unstable**

69. Buchanan specifically discloses that bis(benzene)cobalt ( $\text{Co}(\text{C}_6\text{H}_6)_2$ ) is a “preferred precursor.”

preferred precursors are dimethyl-, diethyl-, or diisobutyl-B,  
Al, Ga, In, As, or Sb hydride;  $\text{Me}_2\text{AlH}(\text{NEtMe}_2)$ ; tertbutyl-  
larsine;  $(\text{Me}_3\text{N})\text{AlH}_3$ ;  $(\text{EtMe}_2\text{N})\text{AlH}_3$ ;  $(\text{Et}_3\text{N})\text{AlH}_3$ ;  
CpWH<sub>2</sub>; Cp<sub>2</sub>MoH<sub>2</sub>; trimethyl-, triethyl-, triisobutyl-, tri-n-  
propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or eth-  
...  
15 pentyl)<sub>4</sub>Cr; Et<sub>3</sub>Pb(neopentoxo); Cp<sub>2</sub>Me<sub>2</sub>Zr; (MeNC)<sub>2</sub>  
PtMe<sub>2</sub>; CpIr(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>; bis Cp-Co, Mo, Fe, Mn, Ni, Ru, V, Os,  
Mg or Cr; bisethylbenzene-, bisbenzene-Co, Mo or Cr;  
triphenyl-Bi, Sb, or As; trivinylboron; trisCp-Sc, Y, La, Ce,  
...  
tatriene) Mo (CO)<sub>3</sub>; NdCp<sub>3</sub>; SmCp<sub>3</sub>; ScCp<sub>3</sub>; TbCp<sub>3</sub>; TiCp;  
25 TmCp<sub>3</sub>; Cp<sub>2</sub>WH<sub>2</sub>; (mesitylene)W(CO)<sub>3</sub>; CpRe(CO)<sub>3</sub>; CpRh  
(CO)<sub>2</sub>; Ir(allyl)<sub>3</sub>; Pt(allyl)<sub>2</sub>; CpIr(cyclooctanedione); [Ir  
(OMe)(cyclooctanedione)]<sub>2</sub>; Ru(cyclooctanedione)(allyl)<sub>2</sub>;  
Ru<sub>3</sub>CO<sub>12</sub>; Fe(CO)<sub>5</sub>; CO<sub>2</sub>(CO)<sub>8</sub>; Ru(CO)<sub>3</sub> (1,3-cyclohexadi-  
ene); Os<sub>3</sub>CO<sub>12</sub>; Cr (CO)<sub>6</sub>; CpCO(CO)<sub>2</sub>; Mn<sub>2</sub>(CO)<sub>10</sub>; CpMn  
(CO)<sub>3</sub>; Mo(CO)<sub>6</sub>; Ni(CO)<sub>4</sub>; Re<sub>2</sub>(CO)<sub>10</sub>; CpRe(CO)<sub>3</sub>; CpRh  
(CO)<sub>2</sub>; Ru<sub>3</sub>(CO)<sub>12</sub>; W(CO)<sub>6</sub>; CpV (CO)<sub>4</sub>; CF<sub>3</sub>CO(CO)<sub>4</sub>;  
30 Pt(CO)<sub>2</sub>(cyclooctanedione); Ir(CO)<sub>2</sub>(cyclooctanedione);  
(CO)<sub>4</sub>Fe[P(OCH<sub>3</sub>)<sub>3</sub>]; (CO)<sub>4</sub>Fe[N(CH<sub>3</sub>)<sub>3</sub>]; CoNO(CO)<sub>3</sub>;  
butoxy, OCH(CF<sub>3</sub>)<sub>2</sub>, OCM<sub>2</sub>(CF<sub>3</sub>), OCM<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>, OSi  
...  
tbutoxy)CuPMe<sub>3</sub>; Pt(PF<sub>3</sub>)<sub>4</sub>; Ni(PF<sub>3</sub>)<sub>4</sub>; Cr(PF<sub>3</sub>)<sub>6</sub>; (Et<sub>3</sub>P)<sub>3</sub>Mo  
(CO)<sub>3</sub>; Ir(PF<sub>3</sub>)<sub>4</sub>; Ti (NO<sub>3</sub>)<sub>4</sub>; Zr(NO<sub>3</sub>)<sub>4</sub>; Hf(NO<sub>3</sub>)<sub>4</sub>; Si(CH<sub>3</sub>)<sub>3</sub>  
(NO<sub>3</sub>); RuNO(NO<sub>3</sub>)<sub>3</sub>; gallium nitrate; Sn(NO<sub>3</sub>)<sub>4</sub>; Co(NO<sub>3</sub>)<sub>3</sub>;  
60 VO(NO<sub>3</sub>)<sub>3</sub>; CrO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>; TiCl<sub>4</sub>; HfCl<sub>4</sub>; ZrCl<sub>4</sub>; InCl<sub>2</sub>; ZnCl<sub>2</sub>;

Buchanan at 6:1-61 (emphasis added).

70. Bis(benzene)cobalt is an organometallic compound in which the metal is in the zero oxidation state. The common definition of organometallic compounds requires that one or more of the carbon atoms of a ligand is bonded directly to the metal atom. A POSA would expect that the 18-electron rule, described above, would accurately anticipate the stability of bis(benzene)cobalt. *See* Ex. 2118.

71. Bis(benzene)cobalt has nine valence electrons from the cobalt atom and 12 electrons are added from the two benzene ligands, resulting in 21 electrons. A POSA would recognize that the 21 electrons present in bis(benzene)cobalt runs counter to the 18-electron rule and would anticipate that bis(benzene)cobalt would not be stable. Additionally, a review of the chemical literature reveals that this compound has never been isolated as a pure compound. The only report of its preparation comes from a matrix isolation study which notes that bis(benzene)cobalt is thermally unstable above -3°C. *See* Ex. 2110, Bechamp at 4, 5, 8.

72. As I discuss further below, this lack of thermal stability violates the requirement that an ALD precursor should exhibit thermal stability at the substrate temperatures and renders bis(benzene)cobalt unsuitable for ALD processes. Ex. 1013 at 13-14; *see also* Banerjee Tr. at 42:12-43:19. Indeed, the stability of bis(benzene)cobalt is so low that it cannot be stored in a precursor vessel rendering

it useless as a precursor for CVD as well as ALD. *See also* Banerjee Tr. at 42:19-23 (“You would want the precursor molecule to have enough thermal stability such that it does not degrade under ambient temperature conditions, for example, so that you have enough shelf life.”).

73. Therefore, in my opinion, bisbenzene-Co, cannot be used as a precursor for ALD or CVD because it cannot be stably synthesized or isolated.

## 2. Buchanan Discloses Precursors That Are Not Thermally Stable At The Substrate Temperatures Required For ALD

74. Another characteristic which a precursor must have to be suitable for ALD is thermal stability at the substrate temperature. *See* Ex. 1013 at 13-14. If the substrate temperature exceeds the precursor’s maximum temperature of thermal stability, the precursor will undergo thermal decomposition during film growth resulting in a non-self-limiting deposition process. ALD is defined as a self-limiting film growth, which is what distinguishes it from other CVD processes.

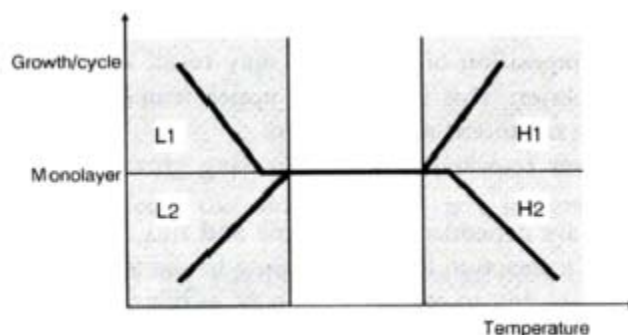


Fig. 12. A processing window of the ALE process. A full monolayer saturation  $f_s = 1$  for both reactants is assumed. Limiting mechanisms in the different areas of the chart are: (L1) condensation of a reactant occurs; (L2) activation energy of a necessary reaction is not exceeded; (H1) decomposition of a reactant results in a non-evaporating surface layer on a monolayer; (H2) re-evaporation of a formed monolayer occurs.

Ex. 2119, Suntola III at 23 (Figure 12).

75. The above figure illustrates Suntola's teaching concerning the effects of temperature on ALD processes, where the optimal temperature region is referred to as the ALD window, which corresponds to the flat portion of the above graph. The ALD window is the temperature region where the growth per ALD cycle is constant as a function of temperature. For a given ALD precursor the temperatures corresponding to the beginning and end of the ALD window depend on the physical properties and chemical reactivity (including thermal stability) of the precursor. Consequently, this flat region, where growth per ALD cycle is constant as a function of temperature, enables consistent growth of single layer films over high aspect-ratio surfaces.

76. In addition to his identification of the ALD window, Suntola identifies four regions in which the growth per cycle is either smaller or larger than that found within the ALD window. Unlike the growth per cycle within the ALD window, these non-ideal regions, identified as L1, L2, H1, and H2 in the above figure, exhibit growth per cycle values that vary measurably with temperature. These changing values of growth per cycle are represented by the solid lines within each of the non-ideal regions shown in the above figure. A POSA would understand that the growth per cycle as a function of temperature for a given ALD

process will follow either L1 or L2 for low temperatures and either H1 or H2 for high temperatures, depending on the process.

77. In the region labelled L1, the growth per cycle increases for some ALD processes as the deposition temperature is lowered. Suntola teaches that the cause of this excessive growth can be attributed to condensation of excess precursor on the surface. A precursor in the gas phase will initially collide with and form a weak bond to the surface. *See* Ex. 2119 at 9. This is referred to as physisorption, and this physisorbed state is the predecessor that can lead to the more strongly bonded chemisorbed state if a possible reaction pathway is available. Suntola teaches that at lower temperatures the weak forces between the gaseous precursor and the substrate, as well as those between the gaseous precursor and other precursors already physisorbed to the surface would lead to condensation of multiple precursor layers. Exposure of this multilayer of precursors to the second reactant would lead to a higher growth per cycle than found in the ALD window.

78. In the region designated L2 in the above figure, Suntola shows that for other ALD processes the growth per cycle decreases with decreasing temperature. Suntola teaches that this depends on the activation energy required for the chemical reaction that converts the physisorbed precursor into the chemisorbed one. As the temperature increases, the fraction of physisorbed precursors that have sufficient thermal energy to overcome the kinetic activation energy barrier leading

to the chemisorbed state will increase. At temperatures below the ALD window, those physisorbed precursors that do not have sufficient thermal energy can instead desorb back into the gas phase thus leading to the formation of an incomplete layer.

79. Further, in the region designated H2 in the above figure, Suntola shows that the growth per cycle for some ALD processes decreases as the deposition temperature increases. Suntola teaches that two effects could contribute to this behavior. First, at higher temperature the precursor is less likely to stay physisorbed to the surface long enough to undergo a chemical reaction leading to a chemisorbed species, thus a complete monolayer is not formed. Second, Suntola teaches that at higher temperatures the already chemisorbed monolayer could desorb from the surface. This would also result in an incomplete monolayer formed each cycle, thus leading to a lower growth per cycle.

80. In the region designated H1 in the above figure, Suntola shows that the growth per cycle increases with increasing temperature. Suntola teaches that this is because at high temperatures the chemisorbed precursors can decompose chemically. At a sufficiently high temperature the activation energy of the thermal decomposition of the precursor complex is exceeded, resulting in the uncontrolled thermal decomposition of the precursor complex. In the region designated H1, the substrate temperature has exceeded the temperature where the adsorbed precursor

is thermally stable. Because the thermal decomposition of the precursor typically results in the precursor complex shedding multiple ligands, the deposition will no longer be limited by the availability of surface binding sites. The result is continuous deposition onto the surface. In region H1, the film growth transitions to a continuous-deposition CVD process. *See Banerjee Tr. at 128:2-129:4.*

81. A POSA would further understand that the shape of the growth per cycle as a function of temperature varies for different precursors and substrates as a function of the precursor's chemical properties, including the binding energy of the precursor to the surface, in both the physisorbed and chemisorbed forms, the activation energy of the reaction between the precursor and the surface, and the chemical reactivity of the precursor, including its thermal stability. Therefore, a POSA would understand that for a given ALD precursor the temperatures corresponding to the beginning and end of the ALD window depend on the physical properties and chemical reactivity (including thermal stability) of the precursor.

82. Further, a POSA would know that the ALD window depends not only on the properties of the precursor but also those of the reactant.

83. A POSA would recognize, therefore, that if the maximum temperature of thermal stability of a precursor complex is below the temperature where condensation through physisorption ceases to be excessive then there is no ALD



window for that precursor. Instead, deposition can only be achieved through deliberate and continuous thermal decomposition of the precursor complex onto the surface, which is a known CVD technique but does not allow for self-limiting monolayer growth and therefore is not ALD nor is it equivalent with ALD.

84. A POSA would recognize that this situation would represent an insurmountable obstacle to using a precursor for ALD, because the temperature cannot simply be increased or reduced to control the reaction the way it can in many other CVD processes. A POSA would understand that this is because, as explained above, the ALD process relies not only on chemical reaction of the precursor but also upon controlled physisorption of the precursor gas, which together allow the formation of a monolayer in a controlled and self-limiting manner.

85. Buchanan identifies several precursors with this property, for which CVD is well-established but which would be unsuitable for ALD because their decomposition temperatures are too low to prevent thermal decomposition during deposition and thereby allow their use in an ALD process.

a. **Buchanan Specifically Discloses The Use Of Dicobalt Octacarbonyl, Which Is Too Thermally Unstable For ALD**

86. Buchanan's identifies dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$  as a "highly preferred" precursor.

Highly preferred precursor source mixtures comprised of at least one carbonyl-containing precursor include:  $\text{Ru}_3\text{CO}_{12}$ ;  $\text{Fe}(\text{CO})_5$ ;  $\text{Co}_2(\text{CO})_8$ ;  $\text{Ru}(\text{CO})_3$  (1,3-cyclohexadiene);  $\text{Os}_3\text{CO}_{12}$ ;  $\text{Cr}(\text{CO})_6$ ;  $\text{CpCo}(\text{CO})_2$ ;  $\text{Mn}_2(\text{CO})_{10}$ ;  $\text{CpMn}(\text{CO})_3$ ; (cycloheptatriene) $\text{Mo}(\text{CO})_3$ ;  $\text{Mo}(\text{CO})_6$ ;  $\text{Ni}(\text{CO})_4$ ;  $\text{Re}(\text{CO})_{10}$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}(\text{CO})_2$ ;  $\text{Ru}_3(\text{CO})_{12}$ ;  $\text{W}(\text{CO})_6$ ;  $\text{CPV}(\text{CO})_4$ ;  $\text{CF}_3\text{CO}(\text{CO})_4$ ;  $\text{Pt}(\text{CO})_2(\text{cyclooctanedione})$ ;  $\text{Ir}(\text{CO})_2(\text{cyclooctanedione})$ ;  $(\text{CO})_4\text{Fe}[\text{P}(\text{OCH}_3)_3]$ ;  $(\text{CO})_4\text{Fe}[\text{N}(\text{CH}_3)_3]$  or  $\text{CoNO}(\text{CO})_3$  where Cp is cyclopentadienyl or substituted cyclopentadienyl wherein replacement of H substituent(s) with methyl, ethyl, isopropyl, n-butyl, sec-butyl,

Buchanan at 12:56-67. Buchanan also discloses the supposed atomic layer deposition of cobalt silicide using  $\text{Co}_2(\text{CO})_8$  and in Example 4 (column 21, lines 4 – 55). It is important to note the details used in this deposition and the results. The preferred substrate temperature range for this experiment is 200 – 800°C, and the  $\text{Co}_2(\text{CO})_8$  precursor pulse time ranged from 0.1 – 1 second and was preferably 0.5 seconds. Silane,  $\text{SiH}_4$ , was used as the silicon reactant pulse. Completion of one ALD cycle consisting of individual pulses of  $\text{Co}_2(\text{CO})_8$ , inert purge, hydrogen, inert purge, silane, inert purge, hydrogen, inert purge was reported to deposit “about 0.4 – 2 monolayers of Co silicide or roughly 0.1 nm.”

87. A POSA would know that this compound is not suitable for use as a precursor for an ALD process due to its low decomposition temperature, i.e., 52°C. Particularly,  $\text{Co}_2(\text{CO})_8$  is a highly reactive, crystalline solid. Its stability was well-known to be limited above room temperature, because  $\text{Co}_2(\text{CO})_8$  decomposes at its melting temperature of 52°C. See, e.g., Ex. 2120, Wender at 5 (Table 1); Ex. 2131, Kodas at 26 (Table 8-8). Thus, a POSA would recognize that at temperatures

necessary for an ALD process  $\text{Co}_2(\text{CO})_8$  will decompose, resulting in CVD style growth.

88. A POSA would know that  $\text{Co}_2(\text{CO})_8$  is sufficiently volatile and has been used as a precursor in CVD processes. *See, e.g.,* Ex. 2121, Gross; Ex. 2122, Dormans. In Gross,  $\text{Co}_2(\text{CO})_8$  was used as a precursor in a CVD process at 200 °C. *See, e.g.,* Ex. 2121 at 2 (Abstract), 3. Gross provides that at 200 °C  $\text{Co}_2(\text{CO})_8$  has a deposition rate of 53 Å/min (5.3 nm/min or 0.9 nm/s), and noted that this rate “remained constant over a 2 h period.” Ex. 2121 at 3; *see also* generally Ex. 2122;. A constant growth rate is characteristic of a CVD process and indicates that exposure of a surface maintained at 200°C to vapors of  $\text{Co}_2(\text{CO})_8$  does not result in self-limited deposition of cobalt atoms and, therefore, is not an example of ALD process.

89. Buchanan purports to disclose an ALD process using  $\text{Co}_2(\text{CO})_8$  in its Example 4. Buchanan at 21:4-55. In my Declaration in Support of Patent Owner’s Preliminary Response I indicated that  $\text{Co}_2(\text{CO})_8$ , though a suitable precursor for CVD, is not suitable for use in an ALD process. Ex. 2101 at ¶118. I understand that in the Institution Decision in IPR2017-00663, the Board indicated that “Example 4 of Buchanan expressly discloses successfully using  $\text{Co}_2(\text{CO})_8$  in an ALD process to form a metal silicide film.” Ex. 2132, IPR2017-00663 Decision at 15-16 (citing Buchanan, 21:4–55, Cert. of Correction). But as discussed below, the

deposition conditions employed in Example 4 of Buchanan would not have resulted in a self-limiting ALD process.

90. Buchanan's Example 4 describes the alternate introduction of  $\text{Co}_2(\text{CO})_8$  and silane,  $\text{SiH}_4$ , into a deposition chamber to form a cobalt silicide. Buchanan at 21:4–55; The substrate within the deposition chamber is heated to  $100^\circ$ – $1200^\circ\text{C}$ , and preferably  $200^\circ$ – $800^\circ\text{C}$ . Buchanan at 21:4–55; The precursor pulse time ranged from 0.1–1 second and was preferably 0.5 seconds, and resulted in “about 0.4 – 2 monolayers of Co silicide or roughly 0.1 nm.” Buchanan at 21:36-42.

91. Based on these conditions, a POSA would recognize that Example 4 is similar to those reported in similar CVD processes using  $\text{Co}_2(\text{CO})_8$ . Particularly, the preferred temperature range in Buchanan begins at  $200^\circ\text{C}$ , which is the same as one of the temperatures studied by Gross et al. and Dorman et al. *See* Ex. 2121, Ex. 2122. Additionally, the substrate temperatures described by Example 4 are well above the decomposition temperature of  $\text{Co}_2(\text{CO})_8$ . *See* Ex. 2120 at 5 (Table 1); Ex. 2131 at 26 (Table 8-8); Banerjee Tr. at 86:3-19 (“Q And based on the notations in the textbooks, is it your understanding that that's above the thermal deposition of cobalt carbonyl? A Yes.”). Thus, a POSA would conclude that the conditions employed in Example 4 of Buchanan would not result in a self-limiting ALD process. In Example 4, deposition of cobalt during the cobalt pulse is no

doubt occurring, however, by limiting the  $\text{Co}_2(\text{CO})_8$  pulse time to 0.5 s, Buchanan is using operator control to limit the CVD of cobalt to approximately a monolayer. A POSA would not mistake this process for true ALD.

92. Therefore, in my opinion, Dicobalt Octacarbonyl cannot be used as a precursor for ALD because it is too thermally unstable at the temperatures of adsorption to allow for an open ALD window.

**b. Buchanan Specifically Discloses Several Additional Metal Carbonyls, Which Are Not Thermally Stable At Substrate Temperatures**

93. Buchanan discloses numerous metal carbonyls, several of which Buchanan specifically identifies as “highly preferred” precursors,

Highly preferred precursor source mixtures comprised of at least one carbonyl-containing precursor include:  $\text{Ru}_3\text{CO}_{12}$ ;  $\text{Fe}(\text{CO})_5$ ;  $\text{Co}_2(\text{CO})_8$ ;  $\text{Ru}(\text{CO})_3$  (1,3-cyclohexadiene);  $\text{Os}_3\text{CO}_{12}$ ;  $\text{Cr}(\text{CO})_6$ ;  $\text{CpCO}(\text{CO})_2$ ;  $\text{Mn}_2(\text{CO})_{10}$ ;  $\text{CpMn}(\text{CO})_3$ ; (cycloheptatriene) $\text{Mo}(\text{CO})_3$ ;  $\text{Mo}(\text{CO})_6$ ;  $\text{Ni}(\text{CO})_4$ ;  $\text{Re}(\text{CO})_{10}$ ;  $\text{CpRe}(\text{CO})_3$ ;  $\text{CpRh}(\text{CO})_2$ ;  $\text{Ru}_3(\text{CO})_{12}$ ;  $\text{W}(\text{CO})_6$ ;  $\text{CPV}(\text{CO})_4$ ;  $\text{CF}_3\text{CO}(\text{CO})_4$ ;  $\text{Pt}(\text{CO})_2$ (cyclooctanedione);  $\text{Ir}(\text{CO})_2$ (cyclooctanedione);  $(\text{CO})_4\text{Fe}[\text{P}(\text{OCH}_3)_3]$ ;  $(\text{CO})_4\text{Fe}[\text{N}(\text{CH}_3)_3]$  or  $\text{CoNO}(\text{CO})_3$  where Cp is cyclopentadienyl or substituted cyclopentadienyl wherein replacement of H substituent(s) with methyl, ethyl, isopropyl, n-butyl, sec-butyl,

Buchanan at 12:56-67.

94. A POSA would know that when carbon monoxide, CO, is attached as a ligand on a metal, it is referred to as a carbonyl. Homoleptic metal carbonyls are a class of organometallic compounds in which the metal is coordinated only by

carbonyl ligands. Polynuclear metal carbonyls, i. e. compounds with more than one metal, include examples such as  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Co}_2(\text{CO})_8$ .

95. Of the metal carbonyls that Buchanan discloses,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Re}_2(\text{CO})_{10}$ , and  $\text{W}(\text{CO})_6$  agree with the 18-electron rule and are sufficiently stable to serve as precursors. They are also sufficiently volatile to serve as precursors. A POSA would know that metal carbonyls have long been known as precursors for CVD processes, since the time of its invention, but metal carbonyls were not recognized as precursors in atomic layer deposition processes leading to metal oxide, nitride or other films. Review articles describing precursors for ALD did not identify metal carbonyls as a class of compounds useful in ALD of metal oxides or for any material. See M. Leskela and M. Ritala, *Requirements for the ALD Precursors*, 9 J. Phys. IV. 837 (1999). Based on the state of the art at the time, a POSA would not expect a metal carbonyl to participate in a self-limiting reaction required for an effective ALD process. For a metal carbonyl to chemisorb to a surface site, loss of at least one CO ligand is required. Once this occurs at elevated temperature, further CO dissociation would eventually result in free binding sites, resulting in chemical vapor deposition of a metal film. In essence, the process would not be self-limiting. The above description of the CVD of cobalt metal is characteristic of the deposition of other metal carbonyls. Even books on ALD published as recently as

2012 did not identify metal carbonyls as a class of precursors useful in ALD. M. Putkonen, *In Atomic Layer Deposition of Nanostructured Materials* at 41, Wiley-VCH: Weinheim ( 2012); *see also* V. Miikkulainen, M. Leskela, M. Ritala, and R.L. Puurunen, *Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends*, 113 J. Appl. Phys. 21301 (2013) (citing 2,389 publications and including figures 7a and 7b entitled “Ligands for ALD metal reactants” but not including carbonyl as a useful ligand). Not only is there no examples of using metal carbonyls in ALD, but also a POSA at the time of the invention would understand the metal carbonyls, while useful in CVD, were not useful for ALD.

96. Therefore, in my opinion, Metal Carbonyls cannot be used as precursors for ALD because they are not capable of self-limited deposition as required for a true ALD process.

**c. Buchanan Specifically Discloses Bis(Benzene)- And Bis(Ethylbenzene)- Complexes Of Molybdenum And Chromium, Which Are Not Thermally Stable At The Substrate Temperature**

97. Buchanan specifically identifies bis(benzene) and bis(ethylbenzene) complexes of molybdenum (Mo) and Chromium (Cr) as “highly preferred” precursors.

Highly preferred precursor source mixtures comprised of at least one alkenyl-containing compound selected from the group consisting of bis Cp Co, Mo, Fe, Mn, Ni, Ru, V, Os, Mg or Cr; bisethylbenzene, bisbenzene Co, Mo or Cr, triphenyl Bi, Sb, or As; trivinylboron, tris Cp Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, D, Ho, Er, Tm, Yb, or Lu; tetraCpTh, Pa, V, Np, Pu or Am; trisallyliridium; CpCr(CO)<sub>2</sub>; Cp<sub>2</sub>ZrMe<sub>2</sub>; CpCuPEt<sub>3</sub>; CpIn; CpIr(cyclooctadiene); CpPd (allyl); CpGaMe<sub>2</sub>; CpGaEt<sub>2</sub>; (cyclohexadiene) FeCO<sub>3</sub>; (cyclooctatetraene)FeCO<sub>3</sub>; ethylferrocene; CpMn(CO)<sub>3</sub>; (cycloheptatriene) Mo(CO)<sub>3</sub>; NdCp<sub>3</sub>; SmCp<sub>3</sub>; ScCp<sub>3</sub>; TbCp<sub>3</sub>; TlCp; Cp<sub>2</sub>WH<sub>2</sub>; (mesitylene)W(CO)<sub>3</sub>; CpRe(CO)<sub>3</sub>; CpRh(CO)<sub>2</sub>; Ir(allyl)<sub>3</sub>; Pt(allyl)<sub>2</sub>; CpIr(cyclooctanedione); [Ir (OMe) (cyclooctanedione)]<sub>2</sub>; or Ru(cyclooctanedione) (allyl)<sub>2</sub> where Cp is cyclopentadienyl or substituted cyclopent-

Buchanan at 11:52-67.

98. While these compounds are known precursors for use in CVD processes, they are not known as precursors for use in an ALD process. This is because, as a POSA would recognize, these compounds are not thermally stable at the substrate temperatures.

99. A POSA would know that unlike bis(benzene)cobalt, discussed above, bis(benzene) and bis(ethylbenzene) complexes of chromium and molybdenum are stable, consistent with the 18-electron rule. A POSA would recognize that to use these compounds in a deposition process, the substrate temperature would need to be high enough such that the compounds would lose one of the two benzene (or ethylbenzene) ligands. However, at the elevated temperature required for the loss of the first benzene (or ethylbenzene) ligand, the remaining metal fragment would



become less stable resulting in the likely loss of the second ligand. This would open sites on the substrate surface for continuous adsorption and reaction of the precursor leading to a chemical vapor deposition process.

100. Therefore, in my opinion, bis(benzene) and bis(ethylbenzene) complexes of molybdenum (Mo) and Chromium (Cr) cannot be used as a precursor for ALD because they are not capable of self-limited deposition as required for a true ALD process.

**d. Buchanan Specifically Discloses Metal-Trifluorophosphine Complexes, Are Not Thermally Stable At The Substrate Temperatures**

101. Buchanan specifically identifies four metal-trifluorophosphine ( $\text{PF}_3$ ) complexes,  $\text{Cr}(\text{PF}_3)_6$ ,  $\text{Ni}(\text{PF}_3)_4$ ,  $\text{Pd}(\text{PF}_3)_4$  and  $\text{Pt}(\text{PF}_3)_4$ , as “preferred” precursors.

Preferred precursor source mixtures are comprised of  $\text{CpCu}(\text{PEt}_3)$ ;  $\text{CpCu}$  (triphenylphosphine); (tert-butoxy)  $\text{CuPMe}_3$ ;  $\text{Pt}(\text{PF}_3)_4$ ;  $\text{Ni}(\text{PF}_3)_4$ ;  $\text{Cr}(\text{PF}_3)_6$ ;  $(\text{Et}_3\text{P})_3\text{Mo}(\text{CO})_3$ ; or  $\text{Ir}(\text{PF}_3)_4$  where Cp is cyclopentadienyl or substituted cyclopentadienyl wherein replacement of H substituent(s) with methyl, ethyl, isopropyl, n-butyl, sec-butyl, tert-butyl, trimethylsilyl or other like substituents dissolved, emulsified or suspended in a  $\text{C}_5\text{--C}_{12}$  alkane liquid with excess of phosphine.

Buchanan at 15:59-67.

102. Metal complexes having a trifluorophosphine ( $\text{PF}_3$ ) ligand exhibit properties somewhat similar to the corresponding metal carbonyls, discussed above. Unlike  $\text{Ir}(\text{PF}_3)_4$ , which I discussed above and which is a nonexistent compound,  $\text{Cr}(\text{PF}_3)_6$ ,  $\text{Ni}(\text{PF}_3)_4$ ,  $\text{Pd}(\text{PF}_3)_4$ , and  $\text{Pt}(\text{PF}_3)_4$  are all known and, consistent with the 18-electron rule, are sufficiently stable and volatile to be used as precursors. Indeed, examples of using these in CVD processes have been published. I am not aware of any examples of using the  $\text{PF}_3$  metal complexes as precursors in ALD processes. As in the case of metal carbonyls, I would expect that at the deposition temperatures dissociation of all  $\text{PF}_3$  ligands would occur leaving the metal atom bound to the surface and, thus, opening new surface sites for the adsorption of more precursor molecules. Because this process will not be self-limiting, the precursors are not useful for ALD.

103. Therefore, in my opinion, metal-trifluorophosphine ( $\text{PF}_3$ ) complexes, including  $\text{Cr}(\text{PF}_3)_6$ ,  $\text{Ni}(\text{PF}_3)_4$ ,  $\text{Pd}(\text{PF}_3)_4$  and  $\text{Pt}(\text{PF}_3)_4$ , cannot be used as a precursor for ALD because they are not thermally stable at substrate temperatures.

**3. Buchanan Discloses Precursors That Are Insufficiently Volatile Or Do Not Chemisorb Onto Or React With The Substrate Surface**

104. Another characteristic which a precursor must have to be suitable for ALD is that it must be able to react and form a strong bond with the substrate surface. See Ex. 1013 at 13-14. A precursor that has formed a strong bond with

the surface is said to be chemisorbed on the surface. *See* Ex. 2119 at 267-68. A precursor in the gas phase will initially collide with and form a weak bond to the surface. *See id* at 269. This process is referred to as physisorption, and this physisorbed state is the predecessor that can lead to the more strongly bonded chemisorbed state if a possible reaction pathway is available.

105. For example, in the well-established ALD system used to form  $\text{HfO}_2$  films,  $\text{HfCl}_4$  in the gas phase will collide with the metal oxide surface coated with OH groups and is initially physisorbed. The physisorbed  $\text{HfCl}_4$  may proceed along two paths. In one path, it may break the weak physisorption bond, and thus desorb back into the gas phase. Clearly, this path will lead to no deposition. In the second path the physisorbed  $\text{HfCl}_4$  will react with available surface OH groups to form a strong Hf-O and release HCl into the gas phase. When all possible surface sites become occupied with  $(-\text{Os})\text{-HfCl}_3$  or  $(-\text{Os})_2\text{HfCl}_2$  groups, where  $(-\text{Os})$  indicates a surface oxide, the surface is saturated and no further change will take place until the gas phase  $\text{HfCl}_4$  is replaced by a pulse of gaseous water.

106. Only molecules that have a chemical reaction pathway for the formation of a strong chemical bond with the surface can chemisorb. Other molecules, which cannot react with the surface, are unable to form these stronger bonds and chemisorb, but instead will inevitably desorb from the surface leaving behind no layer.

107. Buchanan purports to disclose several precursors which in fact do not chemisorb onto the surface. A POSA would understand that such precursors can still be used, in some cases, for CVD by utilizing a thermal decomposition reaction pathway to form the surface layer, but as discussed above this process is not self-limiting and is therefore of no practical interest for ALD processes.

**a. Buchanan Specifically Discloses Several Alkyl-Silanes Which Are Too Unreactive To Use In ALD**

108. Buchanan discloses several alkyl-silanes. For example, Buchanan discloses tetramethyl-, tetraethyl-, tetraphenyl-, and tetra-n-butyl-Si as “highly preferred precursors.”

Highly preferred precursor source mixtures comprised of at least one alkyl-containing compound include: trimethyl-, triethyl-, triisobutyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl-, trineopentyl-, or ethyldimethyl-B, Al, Ga, In, As or Sb; 35  
tetramethyl-, tetraethyl-, tetraphenyl-, or tetra-n-butyl-Si, Ge, Sn, or Pb; dimethyl-, diethyl-, or diisobutyl-B, Al, Ga, In, As or Sb, hydride, chloride, fluoride, bromide, iodide, Cp, amide, dimethylamide or azide; triethyl-, triisobutyl-, 40  
tri-n-propyl-, triisopropyl-, tri-n-butyl- or ethyldimethyl-B, Al, Ga, In, As or Sb trimethylamine, diethylmethylamine, dimethylethylamine, or triethylamine; dimethyl- or diethyl- Zn, Cd, or Hg;(neopentyl)<sub>4</sub>Cr, Et<sub>3</sub>Pb(neopentoxy); Cp<sub>2</sub>Me<sub>2</sub>Zr; (MeNC)<sub>2</sub>PtMe<sub>2</sub>; or CpIr(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> where Cp is 45  
cyclopentadienyl or substituted cyclopentadienyl wherein replacement of H substituent(s) with methyl, ethyl, isopropyl, n-butyl, sec-butyl, tert-butyl, trimethylsilyl or other like substituents dissolved, emulsified or suspended in a C<sub>5</sub>-C<sub>12</sub> alkane liquid. Other preferred precursor source mixtures are 50  
comprised of at least one alkyl-containing compound including, but not limited to: a trimethyl or triethyl substituent emulsified or suspended in a liquid composed essentially of a C<sub>5</sub>-C<sub>12</sub> alkane liquid with optionally added methane or ethane (no more than 30% by volume of the inert liquid). 55

Buchanan at 9:33-55.

109. Alkyl-silanes are remarkably stable compounds. In fact, 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. *See* Ex. 2111, Tiers. NMR 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 “highly preferred precursors” would not work with ALD because they do not readily chemisorb onto surfaces, a process required for ALD.

110. 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 in order to achieve thermal decomposition. *See* Ex. 2109, Herlin. In essence, no pathway exists for the formation of a strong bond to the surface until the temperatures are so high that the molecule is completely decomposed.

111. The thermal stability and lack of reactivity of tetramethylsilane render it useless as an ALD precursor. Consistent with this argument, Hämäläinen et al., reported that attempts to use tetramethylsilane in conjunction with an aluminum precursor for the ALD of aluminum silicate films at temperatures as high as 500 °C were unsuccessful due to the stability of tetramethylsilane. Ex. 2112, Hämäläinen.

112. Therefore, in my opinion, alkyl-silanes, including tetramethyl-, tetraethyl-, tetraphenyl-, and tetra-n-butyl-Si, cannot be used as a precursor for ALD because they do not chemically react with the substrate surface.

**b. Buchanan discloses Metal-Hydrides Which Are Too Involatile To Use In ALD**

113. Buchanan's "preferred" precursors source mixtures for hydride-containing compounds include compounds with the formula  $MR^1_xR^2_yA_z$  where at least  $R^1$  is a hydride and the metal M is Na, K, Rb, or Cs.

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

55 (i)  $MR^1_xR^2_yA_z$

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;  $R^1$  is a hydride;  $R^2$  is a 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/or halogenated, sulfonated or silylated derivatives thereof,  $R^1$  and  $R^2$  may or may not be identical ligands; A is an optional coordinatively bound ligand selected from the

Buchanan at 8:52-67.

114. However, a POSA would recognize that known hydrides with Na, K, Rb, and Cs (i.e., NaH, KH, RbH and CsH) are nonvolatile, solid state compounds that have high melting temperatures at which point they decompose. As pure materials or as a component in a precursor source mixture, it is not possible to convert these hydrides into a vapor phase species needed for both CVD and ALD

processes. A person skilled in the art would further recognize that one could not add other ligands,  $R^2$  or A, to NaH, KH, RbH or CsH to generate a hydride precursor that is soluble and volatile.

115. Therefore, in my opinion, Na, K, Rb, or Cs hydride, cannot be used as a precursor for ALD because they are not volatile.

**D. Buchanan Does Not Disclose How Each Of The Disclosed Precursors Could Be Used In Any Given ALD Process**

116. ALD processes generally cannot be expanded to use new or different precursors without either a disclosure of the deposition conditions or experimentation. Therefore, a POSA would recognize that different deposition conditions must be disclosed for each different precursor in any given ALD process. A POSA therefore would recognize that Buchanan does not disclose CVD or ALD deposition conditions for all of its disclosed precursors.

**1. ALD Processes Cannot Be Readily Expanded To Use New Precursors Without Extensive Experimentation**

117. Counter to Petitioner's arguments, ALD processes generally cannot be expanded to use new or different precursors without either a disclosure of the deposition conditions or experimentation. As previously discussed, precursor design for ALD is an unpredictable field of chemistry that requires testing.

118. Further, I agree with Petitioner's expert, Dr. Banerjee, that a POSA would know that "when you talk about CVD or ALD processes, you cannot

divorce the molecule from the deposition conditions.” *See* Banerjee Tr. at 65:11-15. This remains true for Buchanan’s “highly preferred” precursors. Banerjee Tr. at 78:14-79:4. I agree with Dr. Banerjee when he testified that even Buchanan’s “highly preferred” precursors do not work for every ALD process. *See* Banerjee Tr. at 78:14-79:4; 98:21-99:2. I further agree with Dr. Banerjee that appropriate deposition conditions are necessary to run a successful ALD process. Specifically, Dr. Banerjee testified that “[y]ou can always choose wrong deposition conditions and the process won’t work” and “[w]hat is highly preferred depends on the context [of the desired deposition application].” Banerjee Tr. at 78:14-79:4; 98:21-99:2.

119. In considering whether one of Buchanan’s disclosed precursors can be used in Buchanan’s Example 3, or any particular ALD process, a POSA would first have to consider additional references and then second would have to test the precursor to determine its suitability. Banerjee Tr. at 73:15-74:14; 96:9-97:6.

120. Again, I agree with Dr. Banerjee that determining whether a particular precursor disclosed in Buchanan could work in ALD would first require a POSA to look up “in standard handbooks” or “other sources” information such as the chemical bond strengths, and the vapor pressure of the precursors. *See* Banerjee Tr. at 73:15-74:6; 96:9-97:6. Finally, I agree with Dr. Banerjee that although this information may give a POSA a place to start, it is not sufficient to determine



whether a precursor would be suitable for use in an ALD process and a POSA would have to test the precursor to determine its suitability. *See* Banerjee Tr. at 74:3-6, 89:14-90:2, 96:9-97:6.

121. Dr. Banerjee testified that when testing precursors for suitability for ALD processes, that not all precursors have the same ALD window, which is part of the reason that testing is needed. Banerjee Tr. at 92:5-12.

122. Thus, in my opinion, a POSA would have concluded that if Buchanan intended to disclose that each and every one of the disclosed precursors worked in any given CVD or ALD process that Buchanan would have disclosed CVD or ALD deposition conditions for each of the disclosed precursors.

**2. Buchanan Does Not Disclose CVD or ALD Deposition Conditions for All of its Disclosed Precursors**

123. Buchanan discloses 17 examples in which he discloses deposition conditions for a handful of specific precursors for a handful of specific corresponding CVD and/or ALD processes. Buchanan at 18:38-29:2. Buchanan mentions only a tiny fraction of all the tens of thousands of disclosed precursors in these 17 examples.

124. As discussed above, a POSA would understand that the disclosed deposition conditions would not translate to new precursors or new CVD or ALD processes. Therefore, a POSA would not understand Buchanan to disclose that

these deposition conditions were intended to be used for all of Buchanan's disclosed precursors.

125. Thus, a POSA would recognize that Buchanan does not disclose CVD or ALD deposition conditions for all of its disclosed precursors. Further, a POSA would know that those precursors could not be assumed to work for CVD or ALD processes.

126. Therefore, in my opinion, a POSA would conclude from this that Buchanan does not disclose that each and every one of the disclosed precursors worked in any given CVD or ALD process.

**3. Buchanan Does Not Disclose Deposition Conditions To Expand Example 3 To Use Each and Every Precursor**

127. Buchanan only discloses deposition conditions for two precursors in Example 3, zirconium nitrate ( $\text{Zr}(\text{NO}_3)_4$ ) and hafnium tertbutoxide ( $\text{Hf}(\text{OC}(\text{CH}_3)_3)_4$ ). Buchanan at 19:66-20:49. A POSA would understand that these disclosed deposition conditions would not translate to new precursors or new CVD or ALD processes. Therefore, a POSA would not understand Buchanan to disclose that these deposition conditions were intended to be used for each and every one of Buchanan's disclosed precursors.

128. Therefore, a POSA would recognize that Buchanan does not disclose deposition conditions for the use of each and every in an ALD process to form a

metal oxide film in Buchanan's Example 3. Thus, a POSA also would not understand Buchanan as disclosing that Example 3 can be expanded to use every precursor disclosed in Buchanan

129. In particular, Buchanan does not disclose deposition conditions for the use of metal dialkylamides in an ALD process to form a metal oxide film in Buchanan's Example 3. Therefore, a POSA would not understand Buchanan to disclose the use of metal dialkylamides in Example 3 to form a metal oxide film. In general, a POSA would not understand Buchanan to disclose the use of metal dialkylamides in an ALD process to form a metal oxide film.

**E. Buchanan Does Not Disclose Or Render Obvious That All Its Precursors Could Be Used in Buchanan's Example 3**

130. In my opinion, Buchanan does not disclose or render obvious that all its precursors could be used in Buchanan's Example 3. A POSA would not be motivated to make such a combination based on the disclosures of Buchanan. Further, while Buchanan discloses that Example 3 is not limited only to those specific precursors disclosed in Example 3, Buchanan provides no guidance regarding the selection or suitability of precursors for use in Example 3 beyond those precursors specifically disclosed in Example 3.

**1. A POSA Would Not Have Been Motivated To Modify Buchanan's Example 3 To Use A Metal Dialkylamide Precursor To Form A Metal Oxide Film**

131. I understand that the Petitioner further alleges that a POSA would have been motivated to modify Buchanan's Example 3 to use a metal dialkylamide precursor to form a metal oxide film. *See* Paper 1 at 49-50.

132. I disagree. As discussed above, a POSA would have recognized that not every precursor disclosed in Buchanan works in a given CVD or ALD process. Therefore, in particular, as POSA would have recognized that not every precursor disclosed in Buchanan would work in Example 3.

133. Example 3 is the only disclosure in Buchanan regarding the formation of a metal oxide film using an ALD process. Example 3 involves the use of two precursor mixtures, one of which includes zirconium nitrate in pentane and the other hafnium tertbutoxide in pentane as metal-containing compounds. *See* Ex. 1005 at 19:60-20:24. Neither of these two precursor mixtures is a metal dialkylamide or even an amino-containing compound.

134. I understand that the Petitioner argues that a POSA 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 Example 3, Buchanan's precursors are suitable for both ALD and CVD processes, and Buchanan teaches that metal dialkylamide precursors are preferable. *See* Paper 1 at 49-50. However, as discussed below, Petitioner's arguments are

unsupported by Buchanan's disclosures and are in direct contradiction with the knowledge of one of ordinary skill in the art.

135. As discussed above, a POSA would have understood that many of Buchanan's disclosed precursors would not work in Buchanan's Example 3. A POSA would recognize that the proposition that tens of thousands of potential precursors would all work for a given ALD process is absurd on its face. Further, a POSA would recognize, in particular, that at least the specific precursors discussed above would not work in an ALD process and therefore would not work in Example 3. Therefore, a POSA would not have understood that each-and-every one of those precursors could be used in Buchanan's Example 3. Similarly, a POSA also would not have understood Buchanan as disclosing that Example 3 can be expanded to use every precursor disclosed in Buchanan.

136. In general, a POSA would not interpret Buchanan's disclosure of these precursors as a disclosure that they are all suitable for use in any CVD and ALD process. Rather, as I explained above, a POSA would interpret Buchanan's list of precursors as identifying that 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 is not limited to use with a single class of metals or ligands.

137. Therefore, in my opinion, a POSA would not have been motivated to modify Buchanan's Example 3 to use a metal dialkylamide precursor to form a

metal oxide film. Further, a POSA would not have understood Buchanan to disclose or render obvious that a metal dialkylamide precursor could be used to modify Buchanan's Example 3 to form a metal oxide film.

**2. Buchanan Provides No Guidance Regarding The Selection Or Suitability Of Precursors For Use In Example 3 Beyond Those Disclosed In Example 3**

138. I understand that the Petitioner relies on the following passage from Example 3 to further allege that Example 3 can be expanded to use every precursor disclosed by Buchanan:

The inventive method described can be expanded to include growth of any multicomponent metal, metal oxide, metal nitride or metal silicide film deposited by atomic layer deposition utilizing two or more different precursor source mixtures or utilizing a precursor source mixture which contains two or more precursors . . . . The inventive method described 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.

*See* Petition at 24-25, 35, 38, 45, 47 (citing Buchanan at 20:50-67).

139. I disagree. In my opinion, a POSA would not agree with Petitioner's interpretation of this passage. A POSA would recognize that this passage provides no guidance regarding the selection or suitability of precursors for use in Example 3 beyond those disclosed in Example 3. As such, a POSA would understand that this passage is meant as a general disclosure that the process in Example 3 is not limited to the precursors used, to the extent that other suitable precursors might exist.

140. A POSA would further understand that, generally, Example 3 can be expanded from forming a multicomponent metal oxide as specifically described in Example 3, to forming a single metal oxide by "utilizing one precursor source mixture which contains only one precursor."

141. While, Example 3 may not be limited to the precursors specifically disclosed therein, Example 3 does not disclose or provide any guidance regarding which precursors would be suitable for use in Example 3. A POSA would not understand Example 3 as including any language disclosing that Example 3 can be expanded to use every precursor disclosed in Buchanan.

142. As discussed above, a POSA would recognize that Buchanan discloses precursors that cannot be used in Example 3, including several of Buchanan's "preferred" and "highly preferred" precursors. For example, as discussed above, a POSA would recognize that Buchanan discloses

tetrakis(trifluorophosphine)iridium,  $\text{Ir}(\text{PF}_3)_4$ , dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$ , bis(benzene)- and bis(ethylbenzene)- Mo and Cr, and tetramethyl-, tetraethyl-, tetraphenyl-, and tetra-n-butyl-Si, none of which can be used in Example 3.

143. I understand that the Petitioner argues that “Buchanan expressly teaches that [metal dialkylamide] precursors are preferable.” Paper 1 at 50. I disagree. 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. *Id.* Buchanan never suggests that Example 3 should or could be modified to use metal dialkylamides.

**F. A POSA Would Have Been Dissuaded From Using Metal Dialkylamides in an ALD Process to Form a Metal Oxide Film Because Metal Dialkylamides Were A Known Source Of Impurities**

144. A POSA would have been disinclined to use metal dialkylamides for forming a metal oxide film using an ALD process because a POSA 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. Such impurities would degrade the quality of the resultant metal oxide films e.g., in electronic applications they increase the leakage current. Banerjee Tr. at 130:11-21. A reactive, volatile and thermally stable precursor



would still be unsuitable if it also contributed unacceptable amounts of contaminants or was not compatible with the deposition conditions.

145. Throughout the field of materials science, it has long been recognized that the presence of impurities, even in trace (<1%) amounts, in a solid can alter properties. Intentional incorporation of controlled amounts of impurities, often referred to as doping, is widely used to adjust properties such of electrical conductivity. One skilled in the art of microelectronic manufacturing would understand that great care must be taken to avoid introducing unintentional impurities at every step in the manufacturing process. Chemical precursors used in CVD and ALD can be sources of impurities. In recognition of this fact, chemical firms responsible for manufacturing compounds responded to the need for higher purity precursors by introducing “electronic grade” products. For example, the widely used ALD precursor trimethylaluminum is available from Sigma-Aldrich as technical grade (97% pure) or electronic grade (99.999% pure). Even with electronic grade precursors, the ligands attached to the metal provide another source of unintentional contamination.

#### **1. Carbon and Nitrogen Impurities In Metal Oxide Films From Dialkylamido Ligands**

146. For example, tetrakis(ethylmethyldamido)hafnium, abbreviated TEMAH, has twelve carbon, four nitrogen and thirty-two hydrogen atoms for

every hafnium. Incorporation of even a small fraction of carbon or nitrogen into a  $\text{HfO}_2$  film can impact dielectric properties critical to the optimum functioning of a microelectronic device. In  $\text{HfO}_2$  films, ALD conducted by Kamiyama et al. (Ex. 2125) at  $200^\circ\text{C}$  using TEMAH with ozone as the oxygen resulted in films containing  $1.2 \times 10^{21}$  and  $8 \times 10^{20}$  carbon and nitrogen atoms per  $\text{cm}^3$ , respectively. Despite the small concentrations, these impurities led to undesirable higher values of leakage current and a lower capacitance.

147. While ligands are required to stabilize a metal and render it sufficiently volatile for CVD or ALD processes, scientists and engineers have long recognized that effective precursor design requires an efficient reaction pathway for releasing the ligands back to the gas phase where they can be purged from the reactor. For the deposition of compound films, *i.e.* films comprising two or more elements such of  $\text{TiO}_2$  or  $\text{SiC}$ , researchers focused on precursors in which the nonmetallic element (carbon, nitrogen, oxygen, etc.) was directly bonded to the metal. For instance, methyltrichlorosilane ( $\text{Cl}_3\text{SiCH}_3$ ) was widely used in CVD to deposit silicon carbide ( $\text{SiC}$ ). Another widely used example is tetrakis(isopropoxo)titanium,  $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$ , which is used to deposit  $\text{TiO}_2$  films. In 1975, Sugiyama et al used dialkylamido metal complexes in CVD to deposit metal nitride films. *See* Ex. 2114. Sugiyama's decision to focus on dialkylamido metal complexes was clearly stated. "Dialkylamides of metals are of particular

interest with respect to the fact that they have direct metal-nitrogen  $\sigma$ -bonds, and controlled thermal decomposition of these organometallics could result in the deposition of the corresponding nitrides at temperatures much lower than the conventional preparation techniques...”. For the nitrides of titanium, zirconium and niobium Sugiyama, et al., reported that a “small quantity of carbon” was present, but no quantitative results were included. In fact, later quantitative studies of the carbon content from films deposited using dialkylamido metal complexes established that the “small amount” was in the range of 30 - 50 atomic percent. *See* Ex. 2103; Ex. 2126. Moreover, Fix, et al., report that there was more carbon in the films than nitrogen. Ex. 2103. A POSa would understand that these early reports cast an unfavorable light on the use of dialkylamido metal complexes for use as precursors. These results teach away from their use in CVD and ALD because of their tendency to incorporate carbon into the film.

148. Dubois, et al., reported a detailed study of the reactions of tetrakis(dimethylamido)titanium, TDMAT, with surfaces. *See* Ex. 2105. At 300K (approximately room temperature) TDMAT adsorbs as an intact molecule on a clean titanium disilicide surface. As the temperature is raised, they report “Significant changes in the spectra are seen at ~400 K [127°C]” and conclude that “the molecule is decomposing on the surface”. One skilled in the art would recognize that the nature of the surface will play an important role in determining

the temperature at which decomposition occurs. Nevertheless, this detailed study reinforces the concern that decomposition of the dialkylamido ligands would lead to carbon contamination in metal nitride films and both carbon and nitrogen contamination in metal oxide films.

149. In conclusion, a POSA would understand 1) that even small amounts of impurities can impact the performance of a film, 2) that ligands needed to make precursors volatile can be a source of impurities, and 3) dialkylamido ligands are a source of carbon contamination in metal nitride films and both carbon and nitrogen contamination in metal oxide films.

150. Therefore, in my opinion, a POSA would have been dissuaded from using dialkylamides in an ALD Process to form a metal oxide film because metal dialkylamides were a known source of impurities.

**G. Buchanan Does Not Render Claims 1-3, 5-7, or 9-10 Obvious**

151. For all the reasons discussed above, in my opinion, Buchanan does not render claims 1-3, 5-7, or 9-10 obvious, either alone or in combination with Min and/or Shin, which I discussed in my previous Declaration.

### VIII. OPINIONS ON IPR2017-00664

#### A. U.S. Patent No. 6,537,613, “Process For Metal Metalloid Oxides And Nitrides with Compositional Gradients” (“Senzaki”)

152. As discussed in my previous declaration, and incorporated herein by reference, 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 by varying the temperature of deposition from a first temperature to a second distinct temperature. *See* Senzaki at Abstract; 2:33-57; 3:40-46; and 6:27-34; Banerjee Tr. at 102:3-14; Institution Decision at 6 (“In the process of Senzaki, . . . [t]he temperature of the deposition is [] varied by at least 40° C to deposit a metal/metalloid compound layer have a compositional gradient.”)

153. As the Petitioner provides:

According to Senzaki, when fabricating gate oxides, interlayer dielectrics, and other electronic materials “in the field of electronic materials for device fabrication,” “it is desirable to have materials which have a varying compositional gradient of mixed metals or metal/metalloid composition in either oxide, oxynitride or nitride form.” [Senzaki], 2:18-23. However, Senzaki asserts that the prior art

had not developed a reliable method for controllably producing such a compositional gradient. *Id.*, 2:24-28.

Petition at 22.

154. “Senzaki addresses the purported failure of the prior art to provide a desirable method for controllably producing a mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer.” Ex. 1003, Banerjee Decl. at ¶97 (citing Senzaki at 2:24-28).

155. A POSA would recognize that it was a goal of Senzaki to produce films with mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer. *See* Banerjee Tr. at 102:15-13:7; Banerjee Decl. at ¶97. In the formation of a gate dielectric or insulator such as in a MOSFET, “typically you want a high silicon content close to the silicon substrate interface from a device point of view. And reduce the silicon content and increase [the metal] content as you move further away from the interface.” *See* Banerjee Tr. at 104:22-20. The way Senzaki achieves this, in its described “present invention,” is by changing the temperature during deposition of the gate dielectric layers. *See* Banerjee Tr. at 104:22-20.

156. More specifically, Senazki discloses a five-step process to a produce film with mixed metal/metalloid oxide, oxynitride, or nitride film with a

compositional gradient over the depth of the deposited layer. *See* Senzaki at Abstract; 2:33-57; Banerjee Tr. at 109:15-110:19. Senzaki discloses,

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, comprising:

a) providing two or more metal-ligand and metalloid-ligand complex precursors, which preferably constitute a liquid at ambient conditions, wherein the ligands are preferably the same and are preferably selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, pyrazoles, and their fluorine, oxygen and nitrogen substituted analogs;

b) delivering the mixture to a deposition zone where the substrate is located;

c) contacting the substrate under deposition conditions with the precursors, where the contacting the substrate under deposition conditions is preferably selected from the group consisting of chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition;

- d) varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40° C[] from said first temperature during the contact, and
- e) depositing a multiple metal and metalloid compound layer on the substrate from the precursors resulting in the compositional gradient of the metal and metalloid in the layer as a result of step d).

Senzaki at 2:33-57 (emphasis added).

157. “[T]he overarching goal [of Senzaki] is to achieve a gate insulator, gate dielectric where you can control the relative ratios of silicon-containing species versus in this case the transition metal-containing species. And that’s governed by device requirements. And the way [Senzaki] achieved that as described in Senzaki is by adjusting the deposition temperature.” Banerjee Tr. at 115:7-17.

158. A POSA would understand that Senzaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions.” Senzaki at 3:63-4. The “[a]ppropriate choice of precursors, in the presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxyni-trides.” Senzaki at 3:62-66 (emphasis added).



159. While Senzaki identifies additional deposition techniques, it describes the “present invention,” including each of its examples, as using CVD processes. Senzaki at 3:3-6, 5:10-6:21 (Examples 1-4). Senzaki’s process uses two or more metal-ligand and metalloid-ligand complex precursors in a mixture. *See* Senzaki at Abstract, 2:33-57; 5:10-6:21 (Examples 1-4); Banerjee Tr. at 108:22-109:11 (acknowledging that Senzaki’s Example 1 uses premixed mixtures of precursors). 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.” Senzaki at 3:3-6. Senzaki identifies that DLI in CVD processing “is preferred for the consistent delivery of multi-components because it delivers the same ratio of the constituents in the reactor as in the source container. DLI has the added advantage of storing precursor at room temperature and heating only the amount required for delivery, therefore improving precursor shelf life. So you keep the main part of the reactants at the ambient temperature, you don’t heat that up. And thereby you minimize the thermal decomposition and thereby improve the shelf life of the reactor.” Banerjee Tr. at 112:11-113:18.

**B. Senzaki Does Not Disclose Which, If Any, Of Its Precursors Are Suitable For Use in an ALD Process**

160. As the Board recognizes, “Senzaki does not disclose an explicit example of forming a metal oxide layer using a metal alkylamide in an ALD process.” Institution Decision at 10.

161. I understand that the Petitioner incorrectly alleges that Senzaki discloses that its processes can be implemented using ALD and that a POSA would have implemented Senzaki’s Example 1, which uses a metal alkylamide, using ALD. *See, e.g.*, Petition at 34 (citing Senzaki at 3:40-44 (referring to Example 1), 4:4-15, 5:11-42 (Example 1)). However, a POSA would not have understood Senzaki as disclosing an ALD process using a metal alkylamide precursor.

162. Additionally, as the Petitioner recognizes, the deposition process required by claims 1, 2, 7, and 10 is a self-limiting ALD process with a specific type of precursor to form a specific type of insulator film. Petition at 29.

“Petitioner concedes that Senzaki does not explicitly state that the depositions of the first precursor and the second reactant are self-limiting.” Institution Decision at 9 (citing Petition at 31-35).

163. I understand that in an attempt to cure the deficiencies of Senzaki, Petitioner argues that a POSA would modify Senzaki’s process in view of Min. *See* Petition at 37. I disagree. As discussed in more detail below, a person of

ordinary skill in the art would not have combined the teachings of Senzaki and Min to arrive at a self-limiting ALD process using a metal alkylamide precursor to deposit a metal oxide film.

164. I understand that the Petitioner further asserts, in its description of Senzaki, that Senzaki states that the film formed by CVD in Example 1 could also be formed by ALD. Petition at 24 (citing Senzaki at 4:4-9). The Board also relies on this passage of Senzaki to conclude that “Senzaki explains that the disclosed precursors could also be deposited by atomic layer deposition.” Institution Decision at 6 (citing Senzaki at 5:50, 4:4-9). However, a POSA would not consider Senzaki as providing a blanket disclosure that its precursors could also be deposited by ALD. I understand that Petitioner’s expert, Dr. Banerjee, identified that to determine whether one of Senzaki’s precursors could be used in ALD, a POSA would need to first look at information in available references and then “of course, at the end of the day, [a POSA] would have to do some experimentation.” Banerjee Tr. at 117:18-118:4, 142. I agree with Dr. Banerjee. A POSA would not be able to determine which of Senzaki’s precursors could be used in ALD simply by their identification in Senzaki. In considering whether one of Senzaki’s precursors can be used in an ALD process, a POSA would first have to consider additional references and then second would have to test the precursor to determine its suitability.

165. A POSA would understand that the precursor chemistry involved in the formation of a film via an ALD process is unpredictable. As such, a POSA would not understand Senzaki's identification that techniques other than CVD, such as ALD, may be used as identifying that these techniques are suitable for use with each precursor. Senzaki at 2:44-50; 4:4-15 (identifying low pressure CVD, atmospheric pressure CVD, sub-atmospheric pressure CVD, plasma, photo, radical, or laser enhanced CVD deposition, and jet vapor deposition well recognized deposition techniques, and atomic layer deposition as potentially suitable techniques for the disclosed process). Rather, a POSA would understand, as Senzaki specifically provides, that the “[a]ppropriate choice of precursors, in the presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxyni-trides.” Senzaki at 3:62-66 (emphasis added).

166. Senzaki does not state that its precursors, including those used in its Example 1, can be used for both CVD and ALD, but rather asserts that techniques other than CVD, such as ALD, may be used, provided that there is an “[a]ppropriate choice or precursors” and deposition conditions. Senzaki at 3:63-4:9. Senzaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions.” Senzaki at 3:63-4. However,

Senzaki does not disclose any particular precursor as suitable for ALD or disclose the set of ALD conditions necessary to run a successful ALD process.

167. For example, as the Board acknowledges, while Senzaki describes the use of precursor source mixture metal including a metal alkylamide,  $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$  and  $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ , in a CVD process in Example 1, “Senzaki does not disclose an explicit example of forming a metal oxide layer using a metal alkylamide in an ALD process.” See Institution Decision at 10. In fact, Senzaki does not disclose a single example of an ALD process or provide any guidance regarding which of its disclosed precursors would be suitable for an ALD process.

168. In describing its precursors, Senzaki identifies that the metalloid is preferably silicon, but may be boron, silicon, arsenic, tellurium, or a mixtures thereof. Senzaki at 4:60-62. “The metal is selected from any metal of the Periodic Table of the Elements” (*Id.* at 4:63-64 (emphasis added)) and is preferably,

zinc, cadmium, mercury, aluminum, germanium, gallium, indium,  
thallium, tin, lead, antimony, bismuth, lithium, sodium, potassium,  
rubidium, cesium, beryllium, magnesium, calcium, strontium, barium,  
scandium, yttrium, lanthanum, titanium, zirconium, hafnium,  
vanadium, niobium, tantalum, chromium, molybdenum, tungsten,  
manganese, technetium rhenium, iron, ruthenium, osmium, cobalt,

rhodium, iridium, nickel, palladium, platinum, copper, silver, gold,  
cerium and mixtures thereof.

Senzaki at 4:63-5:7.

169. The ligands may be from any one of fourteen (14) classes of ligands,  
selected from the group consisting of

alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates,  
cyclopentadienyls, carbonyls,  $\beta$ diketonates  $\beta$ ketoiminates,  
 $\beta$ diiminates, pyrazoles and their fluorine, oxygen and nitrogen  
substituted analogs.

Senzaki at 3:54-61. Senzaki fails to provide any guidance regarding which metal-  
ligand or metalloid-ligand combinations are preferable. Further, the classes of  
ligands identified by Senzaki include numerous permutations. However, Senzaki  
fails to provide any guidance regarding preferred permutations.

170. A POSA would have understood that not every precursor disclosed in  
Senzaki can be used for both CVD and ALD. *See* Banerjee Tr. at 66:18-67:7,  
74:15-23. A POSA would also understand that when designing a CVD or ALD  
process, one must consider the precursor and deposition conditions. *See* Banerjee  
Tr. at 65:11-14 (“when you talk about CVD or ALD processes, you cannot divorce  
the molecule from the deposition conditions.”) I agree with Dr. Banerjee that  
appropriate deposition conditions are necessary to run a successful ALD process.

Specifically, Dr. Banerjee testified that “[y]ou can always choose wrong deposition conditions and the process won’t work” and “[w]hat is highly preferred depends on the context [of the desired deposition application].” Banerjee Tr. at 78:14-79:4; 98:21-99:2. Senzaki describes that its desired films may be formed by “using proper precursor mixtures and [deposition] conditions,” but fails to disclose any particular ALD precursor or set of ALD condition. Senzaki at 3:63-4.

**C. A POSA Would Not Have Found It Obvious To Implement Senzaki’s Process Using ALD**

171. I understand that the Petitioner alleges that Senzaki discloses an ALD process using a metal alkylamide precursor. Particularly, Petitioner relies on Senzaki’s disclosure that its process is not specifically limited to CVD and Senzaki’s disclosed CVD process using a metal alkylamide precursor in Example 1, to assert that such a process could be implemented using ALD. *See, e.g.*, Petition at 34 (citing Senzaki at 3:40-44 (referring to Example 1), 4:4-15, 5:11-42 (Example 1)); *see also* Petition at 32-22 (“Senzaki states that its processes can be performed using ALD”) (citing Senzaki at 4:4-15). However, a POSA would not have understood Senzaki as disclosing or rendering obvious an ALD process using a metal alkylamide precursor.

172. As Petitioner’s expert, Dr. Banerjee, recognizes, Senzaki’s process requires the formation of a metal and metalloid compound layer with a

compositional gradient of the metal and metalloid in the layer. Banerjee Tr. at 102:3-14; *see also* Senzaki at Abstract; 2:33-57; 3:40-46; and 6:27-34. To achieve this, Senzaki describes that its process varies the temperature of deposition from a first temperature to a second distinct temperature. *See* Senzaki at Abstract; 2:33-57; 3:40-46; and 6:27-34; Banerjee Tr. at 102:3-14, 108:6-9; Institution Decision at 6.

173. Example 1 in Senzaki describes a CVD process using a  $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$  and  $\text{Si}[\text{N}(\text{CH}_3)_2]_4$  mixture to form a metal/metalloid film with a compositional gradient described in Senzaki's Example 1. Senzaki at 5:10-42. In attempt to describe how Senzaki's Example 1 could use an ALD rather than a CVD process, Petitioner's expert, Dr. Banerjee, asserts that in order to achieve a compositional gradient, one would "tweak[]" the ratio of the silicon and zirconium during the ALD process. *See* Banerjee Tr. 105:14-106:5. More of the  $\text{Si}[\text{N}(\text{CH}_3)_2]_4$  than the  $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$  would be allowed to flow in the initial stages. *See id.* "But then as you build up the layers towards the latter part of the process, [] you change the temperature and you'd change the ratio of the zirconium containing flux versus the silicon containing flux. You have more of the zirconium-containing precursor flowing to the reactor and less of the silicon-containing precursor." *See* Banerjee Tr. 105:14-106:5. Dr. Banerjee testified that for the ALD process, a POSA would choose a deposition temperature within the



ALD window of both the metal,  $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$ , and metalloid,  $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ , precursors used. *See* Banerjee Tr. at 110:25-111:22.

174. A POSA considering Senzaki would not have found it obvious to implement such an ALD process. Senzaki provides no disclosure of varying the ratio of precursors inserted into the deposition chamber, during the process, and as the temperature is varied. In fact, Senzaki discloses that the precursors are premixed before the deposition process begins. Banerjee Tr. at 108:22-109:11 (acknowledging that Senzaki's Example 1 uses premixed mixtures of precursors). Premixing the precursors would prevent varying the ratio of precursors during deposition. Dr. Banerjee alleges that the precursor could be kept separate, however, such a disclosure is not present in Senzaki. *See* Banerjee Tr. at 108:22-109:11.

175. Additionally, Senzaki provides no discussion of the process conditions necessary to run an ALD process or whether precursors will have overlapping ALD windows. The specification includes the following statement for choosing an appropriate mixture of precursors.

The volatile components are chosen such that:

- 1) They are chemically compatible, therefore, no nonvolatile polymeric or multinuclear species are formed.

- 2) No precipitates are generated due to ligand exchange on the metals or inter ligand reactions.
- 3) The mixtures maintain low viscosity and thermal stability.
- 4) Undesired redox chemistry will not take place (eg.  $M+1 + M'+3 \rightarrow M+2 + M'+2$ ).

Senzaki at 3:6-17. A POSA would recognize that Senzaki does not teach that the precursor mixture (or even the individual components of the precursor mixture) must be capable of self-limited deposition as required in ALD.

176. Further, as discussed in Section VII.C.2, above, a POSA would understand that different ALD precursors can have different ALD windows.

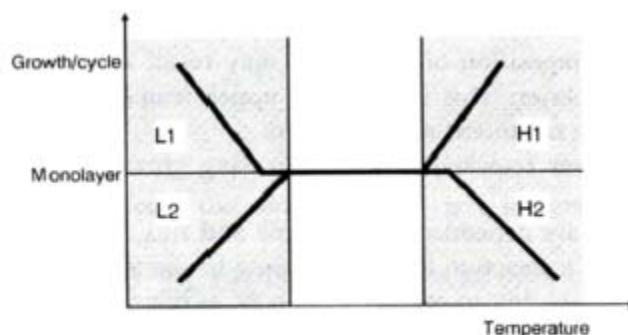


Fig. 12. A processing window of the ALE process. A full monolayer saturation  $f_s = 1$  for both reactants is assumed. Limiting mechanisms in the different areas of the chart are: (L1) condensation of a reactant occurs; (L2) activation energy of a necessary reaction is not exceeded; (H1) decomposition of a reactant results in a non-evaporating surface layer on a monolayer; (H2) re-evaporation of a formed monolayer occurs.

Ex. 2123, Suntola III at FIG. 12. As further discussed above, the range of the ALD window, where the growth per ALD cycle is constant as a function of temperature, depends on the physical properties and chemical reactivity (including the thermal stability) of each given precursor.

177. Petitioner's expert, Dr. Banerjee acknowledges that ALD is self-limiting within the ALD window and asserts that a POSA would choose a common window between the metal and metalloid precursors used. Banerjee Tr. at 29:3-17, 111:6-19. However, Senzaki makes no mention of temperature windows or what precursors could be used together in an ALD process. When asked whether the precursors used in Senzaki's Example 1 has a common window, Banerjee admitted that he did not know. *See* Banerjee Tr. at 110:25-111:22.

178. A POSA would understand that precursors fulfilling the four requirements listed by Senzaki may not be suitable for ALD and may not have ALD windows, let alone ALD windows that overlap with the other precursors in a mixture. Senzaki at 3:6-17. This means that there would be no temperature at which both precursors simultaneously exhibit self-limiting, ALD behavior.

179. For example, a POSA might be motivated to deposit both strontium oxide and copper oxide in a thin film because both metal oxides are present in several high-temperature, superconducting metal oxide films (e. g.  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ ). An ALD window for depositing strontium oxide films using bis(*n*-propyltetramethylcyclopentadienyl)strontium,  $\text{Sr}(\text{PrMe}_4\text{Cp})_2$ , was observed from 250 – 350 °C using a combination of oxygen and water as the sources for oxide in the film. *See* Ex. 2133. A copper oxide ALD process has been reported using (tri-*n*-butylphosphine)copper(I) acetylacetonate, however, this precursor has an ALD

window from 110 – 125 °C using the same oxygen and water mixture as the source of the oxide. *See* Ex. 2134. Although both precursors are likely to fulfill Senzaki's requirements, one would be unable to deposit a mixture of the metal oxides in a self-limited ALD process. Therefore, Senzaki's requirements are insufficient to teach deposition of mixed metal films by ALD.

180. Petitioner's expert, Dr. Banerjee, also ignores potential problems with the simultaneous injection of two precursors. In ALD, simultaneous injection of two precursors would require them to compete for the same surface sites. If one precursor reacts more rapidly with the surface sites, it is possible that it will saturate all of the surface sites before the second precursor has a chance to react. As a result, the composition of the film will depend upon more than just varying the ratio of the precursors introduced into the system.

181. Senzaki does not address the numerous issues faced with designing an ALD process. As a result, while a POSA may not consider Senzaki to be limited to a CVD process, a POSA would not understand Senzaki to disclose or render obvious any particular ALD process, let alone an ALD process as recited by Claim 16 of the '016 Patent.

**D. A POSA Would Understand That Senzaki and Min Have Directly Contrary Goals**

182. A POSA would understand that Senzaki seeks to deposit a film with a compositional gradient by varying the temperature of the deposition process, while Min, on the other hand, seeks to find a stable temperature within an ALD window, to deposit a nitride film through a self-limiting ALD process. Senzaki at Abstract; 2:33-57; 3:40-46; 6:27-34; Min at Abstract, 8; Gladfelter Decl. at ¶¶61

183. A POSA 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. ; Senzaki at Abstract; 2:33-57; 3:40-46; 6:27-34. I agree with Petitioner's expert, Dr. Banerjee testified that "the overarching goal [of Senzaki] is to achieve a gate insulator, gate dielectric where you can control the relative ratios of silicon-containing species versus in this case the transition metal-containing species. And that's governed by device requirements. And the way [Senzaki] achieved that as described in Senzaki is by adjusting the deposition temperature." Banerjee Tr. at 115:7-17 (emphasis added).

184. Varying the temperature to achieve a compositional gradient is central to the teachings of Senzaki, and a POSA would have understood that Senzaki's teachings regarding the temperature change are not limited to the CVD examples

disclosed in Senzaki. Senzaki at 2:33-57; Abstract. In particular, Senzaki does not disclose any other method for achieving a compositional gradient. I agree with Petitioner's expert that Senzaki's process is designed to specifically "address[] the purported failure of the prior art to provide a desirable method for controllably producing a mixed metal/metalloid oxide, oxynitride, or nitride film with a compositional gradient over the depth of the deposited layer." Ex. 1003, Banerjee Decl. at ¶97 (citing Senzaki at 2:24-28). And that, the way Senzaki achieves this, in its described "present invention," is by changing the temperature during deposition of the gate dielectric layers. *See* Banerjee Tr. at 104:22-20.

185. A POSA would understand that Senzaki specifically identifies that its process requires "varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40° C. from said first temperature" for any of its referenced deposition processes, "chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition." Senzaki at 2:33-60. 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. Senzaki at 4:25-28. Each of the examples in Senzaki purposely varies the deposition temperatures. *See* Senzaki 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”).

186. A POSA would understand that Min is directed to an ALD process run at a particular temperature within an ALD window in order to achieve self-limiting deposition. Min teaches as a goal self-limiting deposition as a distinct characteristic of an ALD process. Min at 9. A POSA would understand that Min teaches that in self-limiting deposition, “film thickness per cycle is independent of substrate temperature.” Min at 8. This is achieved by maintaining the deposition temperature within an “ALD window.”

187. 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. *See Banerjee Tr.* at 29:3-6 (“So by ALE or ALD window, you're talking about choosing substrate temperatures and a dose where the growth may be self limiting”). In fact, Fig. 3 of Min depicts such an ALD window in which the deposition rates is independent of deposition temperature. Min at Fig 3, 8 (in case of (a), film thickness per cycle is independent of substrate temperature between 170°C and 210°C.”)

188. As a result, a POSA would understand that the goals of Senzaki are at odds with those of Min. First, a POSA would recognize that Senzaki’s goal of achieving a compositional gradient by varying the deposition temperature is

directly at odds with Min's goal of running an ALD process at a specific temperature within an ALD window to achieve self-limiting deposition. Second, a POSA would recognize that if Senzaki's process were configured to operate at a single temperature or within an ALD window as disclosed by Min, the deposited film would not include Senzaki's desired compositional gradient.

189. I further note that Petitioner's expert, Dr. Banerjee proposes modifying Senzaki's process to use ALD by choosing a deposition temperature within the ALD window of both the metal and metalloid precursors and achieving a compositional ratio by manually controlling the flow ratio of the individual precursors. *See* Banerjee Tr. at 105:14-106:5, 110:25-111:22. A POSA would recognize, however this type of process is not disclosed by either Senzaki or Min. Further, Dr. Banerjee's proposed ALD process includes changing the temperature during the deposition process as the ratio of the precursors is changed. *See* Banerjee Tr. at 105:14-106:5. A POSA would recognize that Min provides no disclosure regarding an ALD process with changing deposition temperatures. And further, if the process temperatures were allowed to vary outside of the ALD window, the process would not be controlled self-limiting ALD as desired by Min.



**E. Senzaki Does Not Render Claims 1, 2, 7, 8, or 10 Obvious**

190. For all the reasons discussed above and/or in my previous declaration, in my opinion, Senzaki does not render claim 1 obvious, either alone or in combination with Min.

191. Further, Senzaki does not render claims 2, 7, 8, or 10 obvious, for the reasons discussed in my previous declaration and further because there claims depend on claim 1, which is not rendered obvious by Senzaki as discussed above.

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

\*\*\*\*

Dated: October 30, 2017

By:



Wayne L. Gladfelter, Ph.D.