

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

LAM RESEARCH CORP.,

Petitioner,

v.

INPRIA CORP.,

Patent Owner.

Case No. IPR2024-00033

Patent No. 9,823,564

**EXPERT DECLARATION OF KAREY HOLLAND, PH.D. IN
SUPPORT OF PETITION FOR *INTER PARTES* REVIEW**

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EXHIBIT LIST

Exhibit	Description
1001	U.S. Patent No. 9,823,564 (“’564 patent”)
1002	Expert Declaration of Karey Holland, Ph.D. (“Holland Declaration”)
1003	U.S. Patent Publication No. 2011/0293888 (“’888 publication”)
1004	U.S. Application No. 12/850,867 Prosecution History (“’867 application PH”)
1005	U.S. Application No. 61/350,103 (“’103 provisional”)
1006	Declaration Sylvia Hall-Ellis, Ph.D. Regarding Authenticity and Public Availability (“Hall-Ellis Declaration”)
1007	’564 Patent Prosecution History (“’564 patent PH”)
1008	Stowers, Jason K. <i>Direct patterning of solution deposited metal oxides</i> . Oregon State University, 2008 (“Stowers 2008”)
1009	U.S. Patent No. 10,782,610 Prosecution History (“’610 patent PH”)
1010	Stowers, Jason, and Douglas A. Keszler. <i>High resolution, high sensitivity inorganic resists</i> . Microelectronic Engineering 86.4-6 (2009): 730-733 (“Stowers 2009”)
1011	Complaint for <i>Inpria Corp. v. Lam Research Corp.</i> , 1-22-cv-01359
1012	Jouve, A., et al. <i>Overcoming pattern collapse of ultra high resolution dense lines obtained with EUV resists</i> . Advances in Resist Technology and Processing XXII. Vol. 5753. SPIE, 2005 (“Jouve”)
1013	Stowers, Jason, Alan Telecky, and Andrew Grenville. <i>Imageable oxides: new solutions for resist</i> . EUVL Symposium. 2010, available at https://euvlsymposium.lbl.gov/pdf/2010/pres/RE-08.pdf (“Stowers 2010”)
1014	Telecky, Alan, et al. <i>Photopatternable inorganic hardmask</i> . Journal of Vacuum Science & Technology B 28.6 (2010): C6S19-C6S22 (“Telecky 2010”)

Exhibit	Description
1015	Summons for <i>Inpria Corp. v. Lam Research Corp.</i> , 1-22-cv-01359
1016	Amador et al. <i>Patterning chemistry of HafSO_x resist</i> . Advances in Patterning Materials and Processes XXXI. Vol. 9051. SPIE, 2014
1017	Reserved
1018	Decker, Shawn R. <i>On the Properties and Characteristics of Solution Processed Hafnium Based Thin-Films from Aqueous Precursors</i> . Oregon State University, 2017
1019	Oleksak et al. <i>Evaluation of Thermal and Radiation Induced Chemistries of Metal Oxo–Hydroxo Clusters for Next-Generation Nanoscale Inorganic Resists</i> . ACS Applied Nano Materials 1.9 (2018): 4548-4556
1020	Reserved
1021	U.S. Patent No. 7,773,365
1022	Stowers et al. <i>Directly patterned inorganic hardmask for EUV lithography</i> . Extreme Ultraviolet (EUV) Lithography II. Vol. 7969. SPIE, 2011 (“Stowers-2011”)
1023	Reserved
1024	Trikeriotis et al. <i>Development of an inorganic photoresist for DUV, EUV, and electron beam imaging</i> . Advances in Resist Materials and Processing Technology XXVII. Vol. 7639. SPIE, 2010 (“Trikeriotis”) (Library Version)
1025	Matsuzawa et al. <i>Theoretical estimation of absorption coefficients of various polymers at 13nm</i> . Journal of Photopolymer Science and Technology 12.4 (1999): 571-576.
1026	Puurunen et al. <i>Hafnium oxide films by atomic layer deposition for high-κ gate dielectric applications: Analysis of the density of nanometer-thin films</i> . Applied Physics Letters 86.7 (2005).
1027	Ober and Giannelis. <i>New oxide nanoparticle extreme-UV photoresists achieve high sensitivity</i> . SPIE Newsroom (2014): 2-4.

Exhibit	Description
1028	<i>Curriculum Vitae</i> of Sylvia D. Hall-Ellis
1029	<i>Curriculum Vitae</i> of Karey L. Holland, Ph.D.
1030	Anderson, Jeremy T., et al. <i>Solution-processed HafSO_x and ZircSO_x inorganic thin-film dielectrics and nanolaminates</i> . <i>Advanced Functional Materials</i> 17.13 (2007): 2117-2124 (“Anderson”)
1031	Trikeriotis et al. <i>Development of an inorganic photoresist for DUV, EUV, and electron beam imaging</i> . <i>Advances in Resist Materials and Processing Technology XXVII</i> . Vol. 7639. SPIE, 2010 (“Trikeriotis”) (Electronic Version)

I. INTRODUCTION

1. My name is Karey Holland. I have been retained by counsel for Petitioner Lam Research Corporation (“Petitioner”) to provide opinions regarding the validity of claims 1-12 (“Challenged Claims”) of U.S. Patent No. 9,823,564 (EX1001, “the ’564 patent”), which I understand is assigned to Inpria Corporation (“Inpria”). I further understand that Petitioner is petitioning for *inter partes* review of the ’564 patent and is requesting cancelation of claims 1-12. My opinions in this expert declaration support Petitioner’s request for *inter partes* review of the ’564 patent and the cancellation of claims 1-12.

II. QUALIFICATION AND BACKGROUND

A. Qualifications

2. I have been involved in the field of photolithography, interconnect technologies, CMP, vacuum technology, reactive ion etch, and metals and dielectric depositions related to semiconductor fabrication for over 35 years. My education, research, and experience in this field is detailed in my curriculum vitae, attached as EX1017 to the Petition.

3. I am co-founder of Techcet and for which I continue to do contract work supporting semiconductor technology roadmaps and wafer forecasting. I am also author of the annual photolithography materials report produced for the Critical Materials Council (a Techcet membership service) and related separate consulting

requests related to photolithography. I also separately consult for two CMP (Chemical Mechanical Planarization) start-up companies.

4. I was previously CTO of Revasum, a SiC polish process and equipment supplier. Before joining Revasum, I was Global Market Sector Manager Semiconductor Process Technology at Edwards Vacuum, VP Process Technology at Mega Fluid Systems, Senior Manager Technology Roadmap at FEI, CTO of NexPlanar, member of the Board of Directors at Nova Measuring Instruments, VP Technology at Thomas West, and CTO and VP of Process Technology IPEC-Westech / SpeedFam-IPEC.

5. I began my career in process engineering at IBM in 1981 where I managed the first 248nm DUV lithography technology development team, and also developed interconnect integration for 4 and 16 Mb DRAMs which were the first chips in the world to use CMP for all interconnect metals and dielectrics.

6. I obtained my Ph.D. in Bio-Analytical Chemistry from Pennsylvania State University, my M.S. in Bio-Analytical Chemistry from Purdue University, and my B.A. in Chemistry from Albion College.

B. Bases for Opinions and Materials Considered

7. In addition to my education, knowledge of the relevant published art, training, and experience, in forming the opinions I provide in this declaration, I have also considered the exhibits in the exhibit list at the front of this declaration.

C. Scope of Work

8. I have been retained by Petitioner as an expert in this matter to provide my various opinions regarding the '564 patent. I receive compensation for my services. No part of my compensation is dependent upon my opinions given or the outcome of this case. I do not have any current or past affiliation with Petitioner, or the named inventors on the '564 patent, or Inpria.

III. LEGAL PRINCIPLES

9. For my opinions in this declaration, I understand that it requires applying various legal principles. As I am not an attorney, I have been informed about various legal principles that govern my analysis. I have used my understanding of those principles in forming my opinions. I summarize my understanding of those legal principles as follows:

10. **Burden of Proof.** I understand that Petitioner bears the burden of proving unpatentability in this proceeding by a preponderance of the evidence. I am

informed that this preponderance of the evidence standard means that Petitioner must show that unpatentability is more probable than not.

11. **Claim Construction.** I have also been told that when I review and consider the claims in the challenged patent that the claim term(s) should be given their ordinary and customary meaning as understood from the perspective of one of ordinary skill in the art at the time of the invention, taking into account the claim language itself, specification, and prosecution history pertaining to the patent, as well as relevant extrinsic evidence. I have applied this standard in formulating my opinions.

12. **Anticipation.** I have been asked to consider the question of anticipation, namely, whether the claims cover something that is new, or novel. I am told that the concept of anticipation requires that each and every element of a challenged claim is present in or otherwise taught by a single reference. I also understand that an anticipatory reference does not need to explicitly describe each element because anticipation can occur when a claimed limitation is necessarily present, inherent or otherwise implicit in the relevant reference.

13. **Obviousness.** I have been asked to consider the question of obviousness. Again, I am told that this analysis must be from the perspective of the person of ordinary skill in the art, and whether such person would consider any

differences between the prior art and what is claimed to have been obvious. To make this assessment, I have been informed that the concept of patent obviousness involves four factual inquiries: the scope and content of the prior art; the differences between the claimed invention and the prior art; the level of ordinary skill in the art; and so-called secondary considerations of non-obviousness.

14. I have further been instructed that one must consider what the person of ordinary skill in the art knew, and what the art taught; suggested; or motivated the person of ordinary skill in the art to further pursue; and to differentiate between steps that were routinely done (such as in response to known problems, steps, or obstacles), and those which, for example, may have represented a different way of solving existing or known problems. Further I have been informed that one cannot use the challenged patent (here, the '564 patent) as a guide from which to select prior art elements, or otherwise engage in hindsight.

15. I am also informed that when there is some recognized reason to solve a problem, and there are a finite number of identified, predictable, and known solutions, a person of ordinary skill in the art has good reason to pursue the known options within his or her technical grasp. If such an approach leads to the expected success, it is likely not the product of innovation but of ordinary skill and common sense. In addition, when a patent simply arranges old elements, with each performing

its known function, and yields no more than what one would expect from such an arrangement, the combination is obvious.

16. I understand that before reaching any final conclusion on obviousness, the obviousness analysis requires consideration of objective indicia of nonobviousness, if offered. These must be considered to ensure that, for example, there were not some unanticipated problems, obstacles, or hurdles that may seem easy to overcome in hindsight, but which were not readily overcome prior to the relevant invention date of the patents/claims at issue here. I understand that these objective indicia are also known as “secondary considerations of non-obviousness,” and may include long-felt but unmet need and unexpected results, among others. I also understand, however, that any offered evidence of secondary considerations of nonobviousness must be comparable with the scope of the challenged claims. This means that for any offered evidence of secondary considerations of non-obviousness to be given substantial weight, I understand the proponent of that evidence must establish a “nexus” or a sufficient connection or tie between that evidence and the merits of the claimed invention, which I understand specifically incorporates any novel element(s) of the claimed invention. If the secondary considerations evidence offered actually results from something other than the merits of the claim, then I

understand that there is no nexus or tie to the claimed invention. I also understand it is the patentee that has the burden of proving that a nexus exists.

17. However, I understand that secondary considerations will not overcome a strong showing of obviousness.

IV. PERSON OF ORDINARY SKILL IN THE ART (“POSA”)

18. As I mentioned above, I have been informed by counsel that my analysis is to be conducted from the perspective of a person of ordinary skill in the art at the time of the invention. I also understand that the person of ordinary skill in the art is assumed to know, understand, and be familiar with all of the relevant prior art, and that such person is a person of ordinary creativity.

19. I have also been informed by counsel that in defining a person of ordinary skill in the art, the following factors may be considered: (1) the educational level of the inventor; (2) the type of problems encountered in the art; (3) prior art solutions to those problems; (4) rapidity with which innovations are made; and (5) sophistication of the technology and educational level of active workers in the field.

20. After considering the above-mentioned factors, it is my opinion that a POSA would have been an individual with at least a graduate degree, such as a masters or Ph.D., in a relevant discipline such as in chemistry, materials science, chemical engineering, physics, or an equivalent field. A POSA would also have 1-3

years of experience in the research, design, development and/or testing of resist materials. I am clearly a POSA and have applied this standard throughout my declaration.

V. THE '564 PATENT

A. Overview of the Described Technology

21. The '564 patent is titled "Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods."

22. The '564 patent describes a number of "aspects" under a section called "SUMMARY OF THE INVENTION." EX1001 at 2:15. "In a first aspect," the '564 patent describes "an aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and ligands comprising peroxide groups, wherein the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the resist composition is stable with respect to phase separation for at least about 2 hours without additional mixing." *Id.* at 2:17-24.

23. "In a further aspect," the '564 describes "a method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising

a polyatomic inorganic anion to form the coating precursor solution.” *Id.* at 2:25-33.

“In some embodiments, the molar concentration ratio of ligands to metal suboxide cations is at least about 2.” *Id.* at 2:31-33.

24. “In other aspects,” the ’564 patent describes “patterned structure comprising a substrate and a patterned inorganic material on a surface of the substrate. The patterned inorganic material can comprise a patterned semiconductor material or a patterned dielectric material, and the patterned inorganic material can have edges with an average line-width roughness no more than about 2.25 nm at a pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.” *Id.* at 2:48-56.

25. In a section called “DETAILED DESCRIPTION OF THE INVENTION,” the ’564 patent states that “[s]ignificant improvements in inorganic precursor solutions provide for superior direct patterning results for inorganic oxide materials comprising polyatomic ions.” *Id.* at 3:66 – 4:1. The ’564 patent states that “[i]n particular, the irradiated coating material can result in a stable inorganic material with a high level of resistance to the developer, e.g., a suitable liquid to dissolve un-irradiated coating material.” *Id.* at 4:17-21. “In some embodiments, the inorganic precursor solution can have a relatively low concentration of metal ions

such that the rheology of the coating composition, e.g., the viscosity, allows the formation of a thin coating on the substrate.” *Id.* at 5:11-14.

26. The ’564 patent explains that “[t]he precursor solution comprises an aqueous solution with metal suboxide cations, radiation sensitive ligands comprising peroxide groups, and polyatomic anions.” *Id.* at 5:45-47. “Specifically, the precursor solution can comprise sufficient radiation sensitive ligands such that the solution has a molar concentration ratio of radiation sensitive ligands to metal suboxide cations of at least about 2 and in some embodiments at least about 5.” *Id.* at 5:61-65.

27. The ’564 patent further explains that “[t]he metal suboxide cations can be selected to achieve the desired radiation absorption.” *Id.* at 6:36-37. In particular, “ ZrO^{+2} based coating materials exhibit good absorption of far ultraviolet light at a 193 nm wavelength. HfO^{+2} based coating materials exhibit good absorption of x-ray radiation and electron beam radiation and can also contribute desirable properties to the coating material, such as density and smoothness.” *Id.* at 6:37-42.

28. The ’564 explains that “[t]o perform the patterning, the precursor solution is generally applied to the entire surface of the substrate or a selected portion thereof.” *Id.* at 7:24-56. “For example, precursor solutions can be coated onto wafers or other substrates using spin coating.” *Id.* at 32-33. Also, “the substrate with the

coating material can be heated to contribute to the removal of solvent.” *Id.* at 7:43-44.

29. The ’564 patent explains that “[t]he coating material generally is radiation sensitive such that exposure to radiation modifies the composition of the coating material at irradiated regions as a latent image.” *Id.* at 7:48-50. According to the ’564 patent, “[t]he radiation absorption results in the condensation of the irradiated portion of the coating material. In other words, the energy from radiation absorption results in agglomeration of the metal ions to change the character of the irradiated material.” *Id.* at 7:57-61.

30. The ’564 patent states that:

it is believed that upon absorption of the radiation, the peroxide functional groups are fragmented, and the composition correspondingly condenses through the formation of bridging metal-oxygen bonds. Through the condensation reaction, the radiation pattern is transferred to a pattern in the coating material. Specifically, there is a pattern of irradiated, and correspondingly condensed, coating material and of un-irradiated coating material, which is substantially unchanged from its composition prior to patterned irradiation of the coating material.

Id. at 7:62 – 8:5.

31. As noted above, the '564 patent states that “any suitable coating process can be used to deliver the precursor solution to a substrate.” *Id.* at 14:8-9. However, “[i]f patterning is performed using radiation, spin coating can be a desirable approach to cover the substrate relatively uniformly, although there can be edge effects.” *Id.* at 14:24-26. The '564 patent explains that a wafer can be spun at rates from about 500 rpm to about 10,000 rpm, in further embodiments from about 1000 rpm to about 7500 rpm and in additional embodiments from about 2000 rpm to about 6000 rpm. *Id.* at 14:26-30.

32. The '564 patent notes that “[t]he spinning speed can be adjusted to obtain a desired coating thickness.” Indeed, according to the '564 patent, “[t]he thickness generally can be a function of the precursor solution concentration, viscosity and the spin speed.” *Id.* at 14:43-45. The '564 patent states that “the coating materials can have an average thickness of no more than about 1 micron, in further embodiments no more than about 250 nanometers (nm), in additional embodiments from about 1 nanometers (nm) to about 50 nm, in other embodiments from about 1 nm to about 40 nm and in some embodiments from about 1 nm to about 25 nm.” *Id.* at 14:47-55.

33. According to the '564 patent, “[t]he coating material can be finely patterned using radiation.” *Id.* at 15:33-34. The '564 patent explains that:

the composition of the precursor solution and thereby the corresponding coating material can be designed for sufficient absorption of a desired form of radiation. The absorption of the radiation results in transfer of energy that breaks the peroxide —O—O— bonds so that at least some of the peroxide-based ligands are no longer available to stabilize the material. With the absorption of a sufficient amount of radiation, the exposed coating material condenses. The radiation generally can be delivered according to a selected pattern. The radiation pattern is transferred to a corresponding pattern or latent image in the coating material with irradiated areas and un-irradiated areas. The irradiated areas comprise condensed coating material, and the un-irradiated areas comprise generally the as-formed coating material.

Id. at 15:34-47.

34. The Examples of the '564 patent exemplify two precursor solutions which are then spin coated onto a wafer to make films. Example 1 “describes a method that has been used to prepare precursor solutions comprising metal suboxide cations based on hafnium (Hf) and/or zirconium (Zr).” *Id.* at 21:14-16.

35. Specifically, “[s]eparate aqueous solutions were prepared ... referred to as Part A for the metal suboxide cations, Part B for the peroxide-based ligand solution and Part C for the solution comprising polyatomic anions.” *Id.* at 21:18-23.

- A solution Part A1 was prepared by filtering a solution of 0.5 mol $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (161.125, Alfa Aesar 99.9%) combined with 500 mL of ultrapure water (18-M Ω ·cm electrical resistance).
- A solution Part A2 was prepared by filtering a solution of 0.5 mol $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (204.76 g, Alfa Aesar 98%) combined with 500 mL of ultrapure water.
- Solution Part B was prepared by diluting $\text{H}_2\text{O}_2(\text{aq})$ (30% w/w, Mallinckrodt Baker) with ultrapure water to yield a 6-8% w/w $\text{H}_2\text{O}_2(\text{aq})$ solution.
- Solution Part C comprised 2-5 M $\text{H}_2\text{SO}_4(\text{aq})$ either obtained in certified concentrations (Fischer Scientific, 10 N) or diluted from concentrated solutions (98% H_2SO_4 , Mallinckrodt Baker) with ultrapure water.

Id. at 21:23-39.

36. The Zr-based and Hf-based precursor solutions were prepared as follows:

Zr precursor solution: “a 30 mL formulation of a Zr based precursor solution with a final zirconium

concentration of 0.16 M was obtained by combining 4.8 mL of solution Part A1 (Zr), 1.8 mL of solution Part B (H_2O_2), 2.16 mL of solution Part C ($\text{H}_2\text{SO}_4(\text{aq})$), and 21.24 mL of ultrapure water.

Hf precursor solution: a 30 mL formulation of an Hf based precursor solution with a final hafnium concentration of 0.15 M was obtained by combining 4.5 mL of solution Part A2 (Hf), 16.875 mL of solution Part B (H_2O_2), 1.8 mL of solution Part C ($\text{H}_2\text{SO}_4(\text{aq})$), and 6.825 mL of ultrapure water.

Id. at 21:57-67.

37. As I noted above, the '564 patent mentions that a ratio of peroxide to metal ion of at least 2 is preferred. The '564 patent also mentions that “generally, the precursor solution comprises a polyatomic ion (e.g., sulfate) concentration from about 0.5 to about 2.0 times the metal suboxide cation concentration.” EX1001 at 11:51-54.

38. Example 1 of the '564 patent does not expressly spell out the ratio of peroxide to Zr ion or peroxide to Hf ion. It also does not expressly spell out the ratio of sulfate ion to Zr ion, or the ratio of sulfate ion to Hf ion. However, the calculations below demonstrate that Zr-based precursor solution has a ratio of 0.66 – 0.88

peroxide group to one Zr ion, and the Hf-based precursor solution has a ratio of 6.25 – 8.33 peroxide groups to one Hf ion.

Calculation for Zr precursor solution:

Part A - $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ $\frac{0.5 \text{ mol}}{0.5 \text{ L}} = \frac{1 \text{ mol}}{\text{L}}$
Part B – 6-8% H_2O_2 <u>6% H_2O_2</u> $\frac{6 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0147 \text{ g H}_2\text{O}_2} = \frac{0.1764 \text{ mol H}_2\text{O}_2}{0.1 \text{ L H}_2\text{O}} = \frac{1.764 \text{ mol H}_2\text{O}_2}{1 \text{ L H}_2\text{O}}$ <u>8% H_2O_2</u> $\frac{8 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0147 \text{ g H}_2\text{O}_2} = \frac{0.235 \text{ mol H}_2\text{O}_2}{0.1 \text{ L H}_2\text{O}} = \frac{2.35 \text{ mol H}_2\text{O}_2}{1 \text{ L H}_2\text{O}}$
Part C – 2-5 M H_2SO_4 $\frac{2 \text{ mol}}{\text{L}}$ $\frac{5 \text{ mol}}{\text{L}}$
Mixture → 4.8 mL Part A + 1.8 mL Part B + 2.16 mL Part C <u>Part A</u> $\frac{1 \text{ mol}}{1 \text{ L}} \times 0.0048 \text{ L} = 0.0048 \text{ mol} = \mathbf{4.8 \text{ mmol}}$

Part B (6% H₂O₂)

$$\frac{1.764 \text{ mol}}{1 \text{ L}} \times 0.0018 \text{ L} = 0.0031752 \text{ mol} = \mathbf{3.1752 \text{ mmol}}$$

Part B (8% H₂O₂)

$$\frac{2.35 \text{ mol}}{1 \text{ L}} \times 0.0018 \text{ L} = 0.00423 \text{ mol} = \mathbf{4.23 \text{ mmol}}$$

Part C (2 M H₂SO₄)

$$\frac{2 \text{ mol}}{1 \text{ L}} \times 0.00216 \text{ L} = 0.00432 \text{ mol} = \mathbf{4.32 \text{ mmol}}$$

Part C (5 M H₂SO₄)

$$\frac{5 \text{ mol}}{1 \text{ L}} \times 0.00216 \text{ L} = 0.0108 \text{ mol} = \mathbf{10.8 \text{ mmol}}$$

Ratio – Zr to PeroxidePart A + Part B (6% H₂O₂)

$$\frac{\text{metal}}{\text{peroxide}} = \frac{4.8 \text{ mmol}}{3.1752 \text{ mmol}} = \mathbf{1.51}$$

Part A + Part B (8% H₂O₂)

$$\frac{\text{metal}}{\text{peroxide}} = \frac{4.8 \text{ mmol}}{4.23 \text{ mmol}} = \mathbf{1.13}$$

The Zr to peroxide ratio is equivalent to 0.66 – 0.88 peroxide per one Zr.

Calculation for Hf precursor solution:

Part A - $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$

$$\frac{0.5 \text{ mol}}{0.5 \text{ L}} = \frac{1 \text{ mol}}{\text{L}}$$

Part B – 6-8% H_2O_2 6% H_2O_2

$$\frac{6 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0147 \text{ g H}_2\text{O}_2} = \frac{0.1764 \text{ mol H}_2\text{O}_2}{0.1 \text{ L H}_2\text{O}} = \frac{1.764 \text{ mol H}_2\text{O}_2}{1 \text{ L H}_2\text{O}}$$

8% H_2O_2

$$\frac{8 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0147 \text{ g H}_2\text{O}_2} = \frac{0.235 \text{ mol H}_2\text{O}_2}{0.1 \text{ L H}_2\text{O}} = \frac{2.35 \text{ mol H}_2\text{O}_2}{1 \text{ L H}_2\text{O}}$$

Part C – 2-5 M H_2SO_4

$$\frac{2 \text{ mol}}{\text{L}}$$

$$\frac{5 \text{ mol}}{\text{L}}$$

Mixture → 4.5 mL Part A + 16.875 mL Part B + 1.8 mL Part CPart A

$$\frac{1 \text{ mol}}{1 \text{ L}} \times 0.0045 \text{ L} = 0.0045 \text{ mol} = 4.5 \text{ mmol}$$

Part B (6% H_2O_2)

$$\frac{1.764 \text{ mol}}{1 \text{ L}} \times 0.016875 \text{ L} = 0.0297675 \text{ mol} = 29.7675 \text{ mmol}$$

Part B (8% H_2O_2)

$$\frac{2.35 \text{ mol}}{1 \text{ L}} \times 0.016875 \text{ L} = 0.03965625 \text{ mol} = \mathbf{39.65625 \text{ mmol}}$$

Part C (2 M H₂SO₄)

$$\frac{2 \text{ mol}}{1 \text{ L}} \times 0.0018 \text{ L} = 0.0036 \text{ mol} = \mathbf{3.6 \text{ mmol}}$$

Part C (5 M H₂SO₄)

$$\frac{5 \text{ mol}}{1 \text{ L}} \times 0.0018 \text{ L} = 0.009 \text{ mol} = \mathbf{9 \text{ mmol}}$$

Ratio – Hf to Peroxide

Part A + Part B (6% H₂O₂)

$$\frac{\text{metal}}{\text{peroxide}} = \frac{4.8 \text{ mmol}}{29.7675 \text{ mmol}} = \mathbf{0.16}$$

Part A + Part B (8% H₂O₂)

$$\frac{\text{metal}}{\text{peroxide}} = \frac{4.8 \text{ mmol}}{39.65625 \text{ mmol}} = \mathbf{0.12}$$

The Hf to peroxide ratio is equivalent to 6.25 – 8.33 peroxide per one Hf.

39. Next, these solutions were spin coated onto wafers according to the method described in Example 2. Specifically:

Five inch silicon wafers were used for substrates.... A wafer was loaded onto a spin coater, and the precursor solution was dispensed onto the center of the wafer. The amount of precursor solution dispensed was selected based

on the desired coating thickness and on the size of the wafer. The spin coater was spun at 100 RPM for 5 seconds to spread the resist across the wafer and then at 3000 RPM for 30-60 seconds to cast the resist film.

EX1001 at 22:4-21.

40. Example 3 “describes a method that has been used to pattern a Zr suboxide based coating material.” *Id.* at 22:33-34. Specifically:

The coating material was deposited at a thickness from 10-50 nm. The Zr-based coating material was irradiated with patterned 193-nm (deep UV) light ... After irradiation, the wafer was passed back to the wafer track and subjected to a post-exposure bake at 40° C. to 200° C. for 1-5 minutes. The exposure with the 193 nm UV light resulted in a patterned coating material. ... FIG. 10 is a pattern of 120-nm pitch lines (approximately 60 nm lines and spaces) in a Zr-based coating material produced by 193-nm lithography at a dose level of 20 mJ/cm².

Id. at 22:35-54.

41. Example 4 “describes a method that has been used to pattern an Hf suboxide based coating material.” *Id.* at 22:59-60. Specifically:

In one embodiment, an Hf-based coating composition was exposed with an electron-beam at 30 keV and about 78

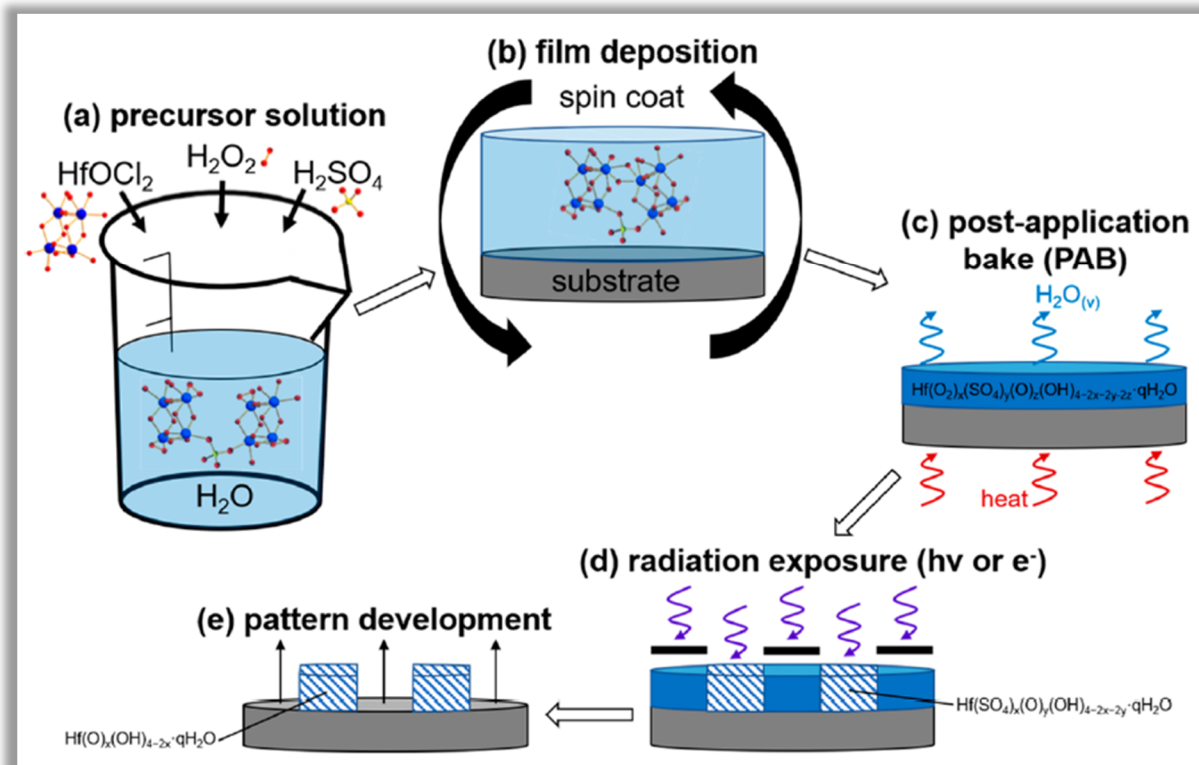
$\mu\text{C}/\text{cm}^2$... FIG. 11 shows 36-nm pitch lines in Hf-based coating material. Another pattern with a pitch of 36-nm is shown in FIG. 12. This pattern was generated with an e-beam dose of $244 \mu\text{C}/\text{cm}^2$.

Id. at 22:63 – 23:7. EUV images were also obtained. Specifically:

The EUV images were obtained using projection lithography with a numerical aperture of 0.25 operating at 13 nm. The resist was applied with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake of 50°C . After exposure at approximately $80 \text{ mJ}/\text{cm}^2$, a post-exposure bake of 75°C . was used prior to development in 25% TMAH. The developed patterns are shown in FIGS. 18A-D. The patterns shown in FIG. 18 have pitches of A) 32-nm, B) 30-nm, C) 28-nm and D) 26-nm.

Id. at 23:33-41.

42. A summary of the Hf-based patterning process is shown below:



EX1019 at Figure 1. As the legend of Figure 1 explains, a precursor solution is formed by combining HfOCl_2 , H_2O_2 , and H_2SO_4 in water. These provide a source of Hf tetramers ($[\text{Hf}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$), peroxide ions (O_2^{2-}), and sulfate ions (SO_4^{2-}). Films are deposited by spin coating and a post-application bake (PAB) removes excess water. Films are then exposed to radiation (photons or electrons) resulting in a solubility decrease in the exposed regions. The pattern is then developed by dissolving unexposed regions in a suitable solvent resulting in a negative-tone image (it could also be positive tone depending on the developer).

B. Challenged Claims

43. As I noted above, I have been asked to provide my opinion on the patentability of claims 1-12 of the '564 patent. I have reproduced the text of those claims below.

44. Claim 1 is an independent claim directed to “[a] structure comprising a substrate and a coating material on a surface of the substrate” as indicated below:

A structure comprising a substrate and a coating material
on a surface of the substrate,

wherein the coating material comprises metal ions with
radiation sensitive ligands and

wherein the coating material has an average thickness
from 5 nm to 30 nm,

wherein exposure of the coating material to UV, EUV
and/or electron-beam radiation alters the chemical
properties of the coating material creating an exposed
coating material with differential dissolution rates
between exposed and un-exposed regions of the coating
material.

45. Claims 2-12 are dependent claims that all depend on claim 1. I understand that this means that to formulate my opinions about the patentability of

claims 2-12, I must evaluate claim 1 in combination with the additional restrictions imposed by claims 2-12. Claims 2-12 recite the following:

2. The structure of claim 1 wherein the metal ions comprise metal suboxide ions.
3. The structure of claim 1 wherein the metal of the metal ions comprises Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.
4. The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.
5. The structure of claim 1 wherein the coating material further comprises polyatomic anions.
6. The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm.
7. The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.
8. The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2.

9. The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C. to 150° C.

10. The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

11. The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

12. The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm².

C. Prosecution History

46. The '564 patent issued from application no. 14/858,612 (“’612 application”) filed on September 18, 2015, and claims priority to application no. 12/850,867 (“parent ’867 application”) (EX1004), filed on August 5, 2010, and provisional application no. 61/350,103 (“’103 provisional”) (EX1005).

The ’612 application was filed with 20 “new” claims. EX1007 at 65. “New” claim 1 of the ’612 application recited:

1. A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average

thickness from about 5 nm to about 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

Id. at 65. “New” claims 2-7 recited:

The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. The structure of claim 1 wherein the metal of the metal ions comprises Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

4. The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. The structure of claim 1 wherein the average thickness is from about 5 nm to about 25 nm.

7. The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

Id. In the “Remarks” accompanying the “new” claims, Inpria stated:

The specification supports new claims 1 and 13, for example, at page 3, lines 9-23, page 5, lines 26-27, page 8, lines 14-17, page 21, lines 16-18 and page 23, line 16 to page 24, line 18. The specification supports claims 2, 4 and 5, for example, page 3, lines 13-15. The specification supports claims 3, 14 and 18, for example, at page 15, line 19 to page 16, line 16 and original claim 10. The specification supports claims 6 and 20, for example, at page 21, lines 16-28. The specification supports claim 7, for example, at page 9, lines 13-25 and page 13, lines 2-5. ... No new matter is introduced by the claims.

Id. at 43.

47. The Examiner issued an “Office Action” on June 30, 2016, rejecting the claims as obvious over Stowers 2009 (EX1010). *Id.* at 126. The Examiner stated that Stowers 2009 discloses “aqueous precursor solutions ... comprising $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{HfOCl}_2 \cdot \text{H}_2\text{O}$, H_2SO_4 , H_2O_2 and purified water ...” *Id.* As to the claimed thickness of “about 5 nm to about 30 nm,” the Examiner stated that Stowers 2009

discloses a coating of “2 nm, which encompasses the instant claimed range of about 5 nm.” *Id.*

48. Inpria filed a response to the office action on September 30, 2016. Inpria argued that the 2 nm disclosure in Stowers 2009 was “line-width-roughness,” not thickness, and that Stowers 2009 disclosed a thickness of 35 nm. *Id.* at 144. In this same response, Inpria cancelled claims 8-20 and added “new” claims 21-25. “New” claims 21-25 recited:

8. The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2.

9. The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C to 150° C.

10. The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

11. The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

12. The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm².

Id. at 405. In the remarks, Inpria stated:

Support for new claim 21 can be found, for example, at page 2, line 30. Support for new claim 22 can be found, for example, at page 22, lines 15-18. Support for new claim 23 can be found, for example, at page 25, line 22-23. Support for new claim 24 can be found, for example, at page 20, lines 10-11. Support for new claim 25 can be found, for example, at page 23, lines 26-30. No new matter is added.

Id. at 141.

49. The Examiner issued another office action on October 18, 2016. In response to Inpria's argument that Stowers 2009 disclosed a thickness of 35 nm (which Inpria argued was outside of the claimed range of about 5 nm to about 30 nm), the Examiner stated that an average thickness of 35 nm is "about 30 nm." *Id.* at 490.

50. Inpria filed a response to the office action on December 19, 2016, in which Inpria amended the claims to remove the term "about." In the remarks, Inpria stated:

With regards to claim 1, the combination of Stowers and Meyers does not teach or suggest a thickness of between about 5 nm and about 30 nm. Rather, Stowers teaches a thickness of 35 nm or greater. Examiner has argued that

35 nm is within the range “about 30 nm.” While applicant maintains the argument that “about 30 nm” is not obvious over Stowers, claim 1 has been amended to remove the term “about” in order to advance prosecution. Therefore, the ranges do not overlap and they are not close enough that one would expect them to have the same properties.

Id. at 508. Notably, Inpria never disputed that, except for the thickness limitation, Stowers 2009 discloses each and every element of pending claim 1 that issued as claim 1 of the '564. *Id.*

51. The Examiner issued another office action on March 1, 2017, in which he withdrew the rejection based on Stowers and Meyers, but maintained another rejection called “nonstatutory double patenting rejection.” *Id.* at 536. After a couple back-and-forth, the Examiner allowed the claims after Inpria filed a “Terminal Disclaimer” to overcome the double patenting rejection. In the “Notice of Allowance,” the Examiner provided the following “examiner’s statement of reasons for allowance.”

No other prior art teaches a structure comprising a coating material comprising metal ions with radiation sensitive ligands, wherein the coating material has an average thickness from 5 nm to 30 nm and wherein the exposure of the coating material to UV, EUV, and/or electron-beam

radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and unexposed regions of the coating material as instantly claimed.

Id. at 587.

VI. CLAIM CONSTRUCTION

52. Claim 8 depends on claim 1 and recites that the claimed structure, i.e., a structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands, has “a metal ion to radiosensitive ligand ratio of at least 2.”

53. The '564 patent specification does not disclose compositions with “metal ion to radiosensitive ligand ratio of at least 2.” Rather, the '564 patent specification states that “the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2.” EX1001 at 2:31-33; 10:2-4 (“In particular, if the mole ratio of peroxide group to the metal cations is at least 2, more stable solutions can be formed.”); 12:11-13 (“Radiation sensitive ligands of particular interest have a peroxide group.”). In other words, the ratio of “at least 2” disclosed the specification is a “ligand to metal” ratio, not the claimed “metal to ligand” ratio.

54. I understand that in certain instances, the Board may correct errors in claims if they are obvious minor typographical and clerical errors in patents through claim construction. To the extent Inpria argues that the Board should correct claim 8 to recite a “radiosensitive ligand to metal ion ratio of at least 2,” I do not believe that this is the kind of error that the Board may correct because it is far from being a minor error.

55. Changing claim 8’s limitation from “a metal ion to radiosensitive ligand of at least 2” to “a radiosensitive ligand to metal ion ratio of at least 2” would drastically change the scope of the claim, because a ligand to metal ratio of “at least 2” is the equivalent to a metal to ligand ratio of “0.5 or less.” Thus, changing the language of claim 8 to recite a ligand to metal ratio would change claim 8’s limitation from “a metal ion to radiosensitive ligand of at least 2” to “a metal ion to radiosensitive ligand of 0.5 or less.” Such change is clearly not a minor adjustment in claim scope.

56. It is also not an obvious error because the claim language is linguistically correct as written—there are no grammatical errors, missing words, misspellings, or similar problems that would make the phrase unreadable or suggest there was an obvious error in the claim language. Moreover, a POSA could reasonably conclude that claim 8 does not recite an error because, as subsequent

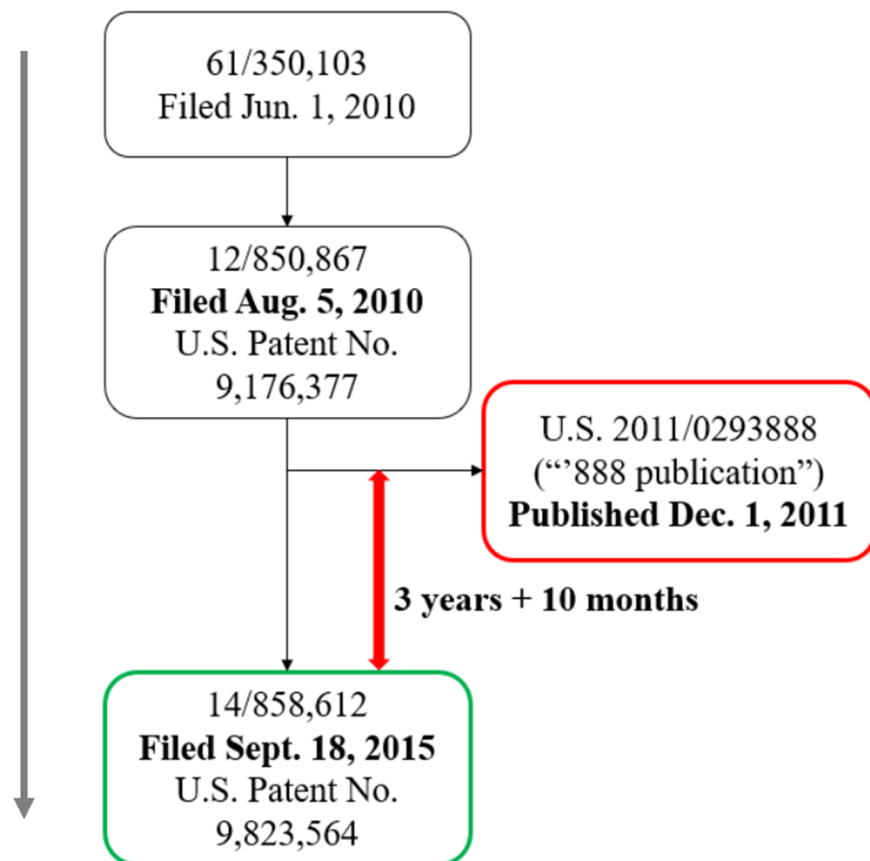
publications from named inventor Douglas Keszler has shown, “[e]ven with excess peroxide in the precursor solution, the Hf:O₂²⁻ ratio saturates near 2:1 in the solution, and it persists in the film.” EX1016 at 5; EX1019 at 5 (“[F]ilms made with at least a 0.5 peroxide to hafnium ratio behave similarly with respect to oxide network formation, confirming that peroxide content in the films does not exceed ≈ 0.5 per hafnium ion.”); EX1018 at 157 (“[T]hin film analysis indicate that the number of peroxide ligands that are able to bind to each hafnium cluster is relatively small, with less than one peroxide group per hafnium ion.”).

57. In other words, in the film, and contrary to the specification’s assertion, the radiosensitive ligand to metal ratio could never reach “at least 2” and in fact, saturates at a ratio of peroxide to metal of 0.5:1, which is the equivalent of the ratio currently recited in claim 8: metal ion to radiosensitive ligand ratio of at least 2.

58. Moreover, as noted above, Inpria first presented the claim that issued as claim 8 on September 30, 2016 (EX1007 at 405), which is after named inventor Keszler reported that the peroxide ligand to metal ratio in the film would never reach 2. *See, e.g.*, EX1016 (published in 2014). Therefore, a POSA could reasonably conclude that claim 8 was intentionally added to capture the ratio that is actually observed in the films, and not what the inventors had written in the specification.

VII. ANALYSIS OF THE PRIORITY DATE OF THE CHALLENGED CLAIMS

59. As noted above, the '612 application, which issued as the '564 patent, was filed on September 18, 2015, and claims priority to the parent '867 application, filed on August 5, 2010, and the '103 provisional. I have reproduced the priority chain below:



60. I have been asked to evaluate whether the Challenged Claims are entitled to a priority date earlier than September 18, 2015, when the '612 application

was filed. As I explain in more detail below, the Challenged Claims should not be given a priority date earlier than September 18, 2015. And if the Challenged Claims are not entitled to claim the benefit of priority to the earlier applications, it is my opinion that all of the limitations of the Challenged Claims are anticipated by the '888 publication, which is the publication of the '867 application.

A. Legal Standards for Determining Priority

61. I have been informed that in the patent application process, an applicant may keep the originally filed claims, or change the claims between the time the patent application is first filed and the time a patent is issued. An applicant may amend the claims or add new claims. These changes may narrow or broaden the scope of the claims. I have been further informed that a patent application is entitled to the benefit of the filing date of an earlier filed application only if the disclosure of the earlier application provides support for the claims of the later application as required by the “written description” requirement. I have been informed that for a patent application to have an adequate written description of the invention it must show the inventor was in possession of the invention at the time the patent application was filed.

62. I have been informed that in order to satisfy the written description requirement one skilled in the art, reading the original disclosure, must immediately

discern the limitation at issue in the claims. In evaluating whether a disclosure provides a sufficient written description, I have been instructed that “one cannot disclose a forest in the original application, and then later pick a tree out of the forest and say here is my invention. In order to satisfy the written description requirement, the blaze marks directing the skilled artisan to that tree must be in the originally filed disclosure.” I have further been informed that it is insufficient if the limitations are obvious variants of the disclosure in the specification.

B. The Parent '867 Application Does Not Disclose the Claimed Thickness Limitations

63. Claims 1 and 6 of the '564 patent recite:

1. A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from 5 nm to 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

6. The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm.

64. The parent '867 application, filed on June 1, 2010, does not contain written description support for the “average thickness” limitations recited in claims 1 and 6. There is nothing in the specification that demonstrates that the inventors believed that a coating with “an average thickness from 5 nm to 30 nm” or “from 5 nm to 25 nm” were part of their invention.

65. The only discussion in the parent '867 application concerning the thickness of the coating is reproduced in its entirety below:

The thickness of the coating generally can be a function of the precursor solution concentration, viscosity and the spin speed. For other coating processes, the thickness can generally also be adjusted through the selection of the coating parameters. In some embodiments, it can be desirable to use a thin coating to facilitate formation of small and highly resolved features. In some embodiments, the coating materials can have an average thickness of no more than about 1 micron, in further embodiments no more than about 250 nanometers (nm), in additional embodiments from about 1 nanometers (nm) to about 50 nm, in other embodiments from about 1 nm to about 40 nm and in some embodiments from about 1 nm to about 25 nm. A person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit

ranges above are contemplated and are within the present disclosure.

EX1004 at 23, lines 16-26.¹

The coating material was produced according to the method of Example 2 with a ZrO^{+2} -based coating composition. The coating material was deposited at a thickness from (sic) 10-50 nm.

Id. at 35, lines 14-15.

The resist was applied with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake of 50° C.

Id. at 36, lines 29-30.

22. The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

Id. at 40, claim 22.

66. It is clear that the parent '867 application does not recite a thickness of 5 nm or 30 nm. It also does not recite a thickness range of 5 nm to 30 nm, as recited

¹ I note that during prosecution, Inpria relied on the specification at page 21, lines 16-26 as providing support for claim 1. EX1007 at 43.

in claim 1. While the parent '867 application does recite a thickness of 25 nm, it does not recite a thickness of 5 nm, or a thickness range of 5 nm to 25 nm, as recited in claim 6. The '103 provisional does not disclose the ranges or the endpoints either, as it only discloses an “optimal thickness range of 20 nm to 40 nm.” EX1005 at 2. There is no direction in the parent '867 application that the inventors gave any import to these specific thickness ranges when they originally filed the application. In fact, the first time that Inpria disclosed these thickness ranges was on September 18, 2015, in the “new” claims filed with the '612 application. EX1007 at 65, 9-18-2015 claims.

67. Moreover, as I noted above, during prosecution of the '612 application (i.e., the '564 patent), Inpria argued that the claimed 5-30 nm thickness range did not overlap with 35 nm, and, moreover, that the thickness values were “not close enough that one would expect them to have the same properties.” EX1007 at 508. In other words, according to Inpria, the 5 nm difference between the 35 nm film thickness of Stowers 2009 and the 30 nm upper value of the claimed thickness range was too much of a difference for a POSA to expect the coatings to have the same properties. If Inpria is correct, then the disclosed range of 1 nm to about 40 nm or from about 1 nm to about 25 nm in the '867 application certainly cannot provide support for the claimed ranges of 5-30 nm and 5-25 nm because thicknesses of 1 nm

and 5 nm or 25 nm and 30 nm “are not close enough that one would expect them to have the same properties.”²

68. Thus, I do not believe that the Challenged Claims should be entitled to a priority date earlier than September 18, 2015, i.e., when the inventors first presented the “new” claims reciting the thickness range limitations.

VIII. THE PRIOR ART

A. '888 Publication (EX1003)

69. U.S. Publication 2011/0293888 (“’888 publication”) was filed on August 5, 2010, and published on December 1, 2011. Because the Challenged Claims should not be entitled to a priority date earlier than September 18, 2015, I understand that the ’888 publication is prior art the Challenged Claims.

² To be clear, I do not believe that there is a meaningful difference between films that are 25 nm, 30 nm or 35 nm thick, such that a POSA would expect them to have different radiation properties. But since Inpria convinced the Examiner that there was a meaningful difference, it seems only fair that Inpria should be kept to its words.

B. Stowers 2008 (EX1008)

70. Stowers-2008 was published by October 21, 2008. I understand that Stowers 2008 is therefore prior art to the '564 patent regardless of the priority date.

C. Stowers 2009 (EX1010)

71. Stowers 2009 was published by December 3, 2008. I understand that Stowers 2009 is therefore prior art to the '564 patent regardless of the priority date.

D. Trikeriotis (EX1024)

72. Trikeriotis was published by March 25, 2010. I understand that Trikeriotis is therefore prior art to the '564 patent regardless of the priority date.

IX. GROUND 1: CLAIMS 1-12 ARE ANTICIPATED BY THE '888 PUBLICATION

73. As noted above, I do not believe that claims 1-12 should be entitled to a priority date earlier than September 18, 2015. As a result, I understand that the '888 publication, which published on December 1, 2011, is prior art to claims 1-12. As shown below, the '888 Publication anticipates claims 1-12 because it discloses each and every element of those claims.

A. Claim 1

1. Preamble: A structure comprising a substrate and a coating material on a surface of the substrate

74. The '888 publication discloses that “the invention pertains to a patterned structure comprising a substrate and a patterned inorganic material on a surface of the substrate.” EX1003 ¶0010.

2. wherein the coating material comprises metal ions with radiation sensitive ligands

75. The '888 publication discloses that “the patterned coating material comprises metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions.” *Id.* ¶0009. The '888 publication also discloses that “[r]adiation sensitive ligands of particular interest have a peroxide group, —O—O—.” *Id.* ¶0059; *id.* ¶0032 (“The coating materials can be designed to be sensitive to selected radiation, such as ultraviolet light and/or electron beams.”); ¶0039 (“Specifically, the precursor solution can comprise sufficient radiation sensitive ligands such that the solution has a molar concentration ratio of radiation sensitive ligands to metal suboxide cations of at least about 2 and in some embodiments at least about 5.”).

3. wherein the coating material has an average thickness from 5 nm to 30 nm

76. In Example 4, the '888 publication “describes a method that has been used to pattern an Hf suboxide based coating material” and “[t]he resist was applied with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake of 50° C.” *Id.* ¶¶0102-0107. The '888 publication also discloses thickness ranges that overlap with the claimed range. ¶¶0068, 0100.

4. wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material

77. The '888 publication discloses that “[t]he method can comprise irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm² or an electron beam at a dose equivalent to no more than about 300 µC/cm² at 30 kV, and contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form the patterned inorganic material.” *Id.* ¶0011. The '888 publication further explains that “the un-irradiated coating material can be relatively more easily dissolved by suitable developer compositions while the exposed coating material can remain appropriately resistant to the developer composition. Since the un-irradiated coating material can

be relatively more easily dissolvable with a developer in comparison with the irradiated coating material, the contact time with the developer can be reduced while still maintaining desired removal of the coating composition.” *Id.* ¶0043.

78. The ’888 publication also discloses that “it is believed that upon absorption of the radiation, the peroxide functional groups are fragmented, and the composition correspondingly condenses through the formation of bridging metal-oxygen bonds. Through the condensation reaction, the radiation pattern is transferred to a pattern in the coating material. Specifically, there is a pattern of irradiated, and correspondingly condensed, coating material and of un-irradiated coating material, which is substantially unchanged from its composition prior to patterned irradiation of the coating material.” *Id.* ¶0046; ¶0075 (“With electron beam lithography, the electron beam generally induces secondary electrons which generally modify the irradiated material.”).

B. Claim 2: The structure of claim 1 wherein the metal ions comprise metal suboxide ions

79. The ’888 publication discloses that “the patterned coating material comprises **metal suboxide cations**, ligands comprising a peroxide group and inorganic polyatomic anions.” *Id.* ¶0009.

C. Claim 3: The structure of claim 1 wherein the metal of the metal ions comprises ...Zr, ...Hf, ...

80. The '888 publication discloses that “Metal suboxide cations of particular interest include, for example, ZrO^{+2} , ZrOOH^+ , $\text{Zr}(\text{OH})_2^{+2}$, $\text{Zr}(\text{OH})_3^+$, HfO^{+2} , HfOOH^+ , $\text{Hf}(\text{OH})_2^{+2}$, $\text{Hf}(\text{OH})_3^+$, combinations thereof and/or combinations with other metal suboxide cations.” *Id.* ¶0056.

D. Claim 4: The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands

81. The '888 publication discloses that “the patterned coating material comprises metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions.” *Id.* ¶0009.

E. Claim 5: The structure of claim 1 wherein the coating material further comprises polyatomic anions

82. The '888 publication discloses that “the patterned coating material comprises metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions.” *Id.* ¶0009.

F. Claim 6: The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm

83. In Example 4, the '888 publication “describes a method that has been used to pattern an Hf suboxide based coating material” and “[t]he resist was applied

with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake of 50° C.” *Id.* ¶¶0102-0107.

G. Claim 7: The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists

84. The '888 publication discloses that “[r]elative to organic resists, the inorganic coating material provides distinct advantages with respect to absorption of selected radiation as well as high contrast between exposed and non-exposed regions such that high resolution can be achieved with moderate radiation doses.” *Id.* ¶0050. Organic resists are “conventional” resists. *Id.* ¶0049 (referring to organic resists as “conventional”); ¶0033 (same). The '888 publication also discloses that “the patterning composition can be sensitive to, for example, ultraviolet light, x-rays or electron beams, as well as a particular wavelength or range of wavelengths within each radiation type.” *Id.* ¶0037; ¶0073 (“The ultraviolet range can be subdivided in several ways under accepted Standards, such as extreme ultraviolet (EUV) ...”). The '888 publication also states that “HfO⁺² provides good absorption of electron beam material and extreme UV radiation.” *Id.* ¶0057.

H. Claim 8: The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2

85. As noted above, specification does not disclose a “metal ion to radiosensitive ligand ratio of at least 2.” Rather, the specification states that “the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2.” EX1001 at 2:31-33. In other words, the specification describes a “ligand to metal” ratio of at least 2, not a “metal to ligand” ratio.

86. To the extent claim 8 contains an “obvious error” that is correctable and should recite a “ligand to metal” as opposed to a “metal to ligand” ratio, then the ’888 publication discloses this limitation. EX1003 ¶ 0007 (“the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2”). Indeed, during prosecution, Inpria identified the specification at “page 2, line 30” reciting a “molar concentration ratio of ligands to metal suboxide cations of at least about 2” as providing support for this claim. EX1007 at 141.

87. If claim 8 does not contain an “obvious error,” Example 1 of the ’888 publication discloses this limitation, because it discloses ZircSO_x precursor solutions with a peroxide to metal ratio of 0.66 – 0.88 and HafSO_x precursor solutions with a peroxide to metal ratio of 6.25 – 8.33. *See* my ratio calculations above.

88. As reported by named inventor Keszler, “[e]ven with excess peroxide in the precursor solution, the $\text{Hf}:\text{O}_2^{2-}$ ratio saturates near 2:1 in the solution, and it persists in the film.” EX1016 at 5. This means that even though the peroxide to metal ratio is more than 0.5:1 in Example 1, the resulting films that are made in Examples 3 and 4 will have a peroxide to metal ratio of 0.5:1, i.e., a metal to peroxide ratio of at least 2.

I. Claim 9: The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C to 150° C

89. The ’888 publication states that “[i]n embodiments in which heat is applied to remove solvent, the coating material can be heated to temperatures from about 45° C to about 150° C.” EX1003 ¶0070.

J. Claim 10: The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent

90. The ’888 publication discloses that “[i]n general, the developer can be aqueous acids or bases.” *Id.* ¶0079. The ’888 publication also discloses that “the irradiated coating material can result in a stable inorganic material with a high level of resistance to the developer, e.g., a suitable liquid to dissolve un-irradiated coating material.” *Id.* ¶0033; ¶0011 (“the invention pertains to a method for forming a patterned structure comprising ... contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form the patterned inorganic

material.”). In other words, the developer does not dissolve the irradiated coating material, and only dissolves the un-irradiated coating material.

K. Claim 11: The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent

91. The '888 publication does not appear to disclose this limitation. However, when Inpria first presented this claim during prosecution (EX1007 at 405), Inpria noted in the Remarks that the support for this new claim could be found “at page 20, lines 10-11” of the specification. *Id.* at 141.

92. The cited passage in the specification recites: “Traditional organic resists are soluble in nonpolar solvents and are deposited onto hydrophobic surfaces.” *Id.* at 26. If Inpria is correct that the cited sentence provides written description support for this claim, then the '888 publication, which also contains this sentence (EX1003 ¶ 0065), anticipates the claim.

L. Claim 12: The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²

93. In Example 4, the '888 publication states:

EUV images were obtained using projection lithography with a numerical aperture of 0.25 operating at 13 nm. The resist was applied with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake

of 50° C. After exposure at approximately 80 mJ/cm², a post-exposure bake of 75° C. was used prior to development in 25% TMAH. The developed patterns are shown in FIGS. 18A-D. The patterns shown in FIG. 18 have pitches of A) 32-nm, B) 30-nm, C) 28-nm and D) 26-nm.

EX1003 ¶0107. In claim 35, the '888 publication discloses “[a] method for forming a patterned structure comprising ... irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm².” The '888 publication further states that “[t]he method can comprise irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm² or an electron beam at a dose equivalent to no more than about 300 µC/cm² at 30 kV, and contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form the patterned inorganic material.” ¶0011; ¶0074 (“The amount of electromagnetic radiation can be characterized by a fluence... Suitable radiation fluences can be from about 1 mJ/cm² to about 150 mJ/cm², in further embodiments from about 2 mJ/cm² to about 100 mJ/cm² and in further embodiments from about 3 mJ/cm² to about 50 mJ/cm².”).

94. Moreover, as I noted above, when Inpria presented the “new” claims during prosecution of the '612 application, it provided “support” for the “new”

claims. Each of the passages cited by Inpria as purportedly providing support for the new claims is found verbatim in the '888 publication as shown below:

'564 Patent Claims	"Support" in the Specification	'888 Publication
Claim 1	Page 3, lines 9-23	¶¶ 0009-0010
	Page 5, lines 26-27	¶ 0032
	Page 8, lines 14-17	¶ 0039
	Page 21, lines 16-18	¶ 0068
	Page 23, line 16 to page 24, line 18	¶¶ 0073-0075
Claims 2, 4 and 5	Page 3, lines 13-15	¶ 0009
Claim 3	Page 15, line 19 to page 16, line 16	¶ 0056
Claim 6	Page 21, lines 16-28	¶ 0068
Claim 7	Page 9, lines 13-25	¶ 0041
	Page 13, lines 2-5	¶ 0050
Claim 8	Page 2, line 30	¶ 0007
Claim 9	Page 22, lines 15-18	¶ 0070
Claim 10	Page 25, line 22-23	¶ 0079
Claim 11	Page 20, lines 10-11	¶ 0065
Claim 12	Page 23, lines 26-30	¶ 0074

X. GROUND 2: CLAIMS 1-5, 7-10 AND 12 ARE ANTICIPATED BY STOWERS 2008

95. Even if the claims are entitled to claim priority to June 1, 2010—which I do not believe they should be able to—claims 1-5, 7-10 and 12 are anticipated by Stowers 2008.

A. Independent Claim 1**1. Preamble: A structure comprising a substrate and a coating material on a surface of the substrate**

96. Stowers 2008 discloses “[a] new system for directly patterning functional metal oxides by UV and EUV.” EX1008 at 65. In Stowers 2008, precursor “solutions were spin coated at 3000 rpm for 30 seconds resulting in films...” *Id.* at 68. “Substrates were either silicon wafer chips (n+ heavily doped) or silicon coupons with 200 nm of thermal oxide.” *Id.* A POSA would understand that the precursor solutions are spin coated onto those silicon wafers, i.e., a substrate. *See, e.g., id.* at 21 (“Depositing a thin uniform coating of photoresist is generally a straight forward process. The photoresist, dissolved in an appropriate solvent, is deposited onto the surface of a wafer located on a turntable. The wafer is then spun to a high RPM, which ejects excess material from the lip of the wafer to leave a thin and uniform film layer that is depleted in solvent.”).

97. Stowers 2008 therefore discloses a “structure comprising a substrate and a coating material on a surface of the substrate.”

2. wherein the coating material comprises metal ions with radiation sensitive ligands

98. As noted above, Stowers 2008 discloses spin coating precursor solutions onto wafers. The precursor solutions of Stowers 2008 were prepared by:

combining the ZrOCl_2 (aq) or HfOCl_2 (aq) with H_2O_2 (aq) to give a metal to peroxide ratio of 1 to 0.75. The solution was allowed to rest for 15 min. to enable ligand exchange to approach equilibrium. Following this, H_2SO_4 (aq) was added to give a metal to sulfate ratio of 1 to 0.5-0.7. Again the solution was allowed to rest for 15 min to enable ligand exchange to reach equilibrium.

Id. at 68.

99. These “[w]orking solutions were spin coated at 3000 rpm for 30 seconds resulting in films 30 to 35-nm thick.” *Id.* POSA would understand that the “working solutions” of Stowers 2008 contain “metal ions,” since, in solution, ZrOCl_2 and HfOCl_2 exist as ZrO^{2+} and HfO^{2+} , *i.e.*, metal suboxide ions. *See, e.g.*, EX1021 ¶0009 (“hafnium suboxide (HfO^{2+}), may be provided by providing an aqueous solution of hafnium oxy chloride ($\text{HfOCl}_2(\text{aq})$).”). Since those precursor solutions in Stowers 2008 are spin-coated onto wafers to make films, the resulting films will necessarily also contain those same metal ions.

100. A POSA would also understand that the peroxide group in the working solutions of Stowers 2008 is a radiation sensitive ligand. For example, Stowers 2008 states that “both ZircSOx and HafSOx are UV sensitive” and that “[t]he extinction coefficients of these materials have previously been determined.” EX1008 at 69.

Stowers 2008 then notes that “[i]t is expected that these extinction coefficients will be different with the presence of peroxide in the as-deposited material...” *Id.* An extinction coefficient is a property that determines how strongly a material absorbs radiation at a particular wavelength. Thus, Stowers 2008 teaches that the peroxide group is radiation sensitive because Stowers 2008 indicates that the extinction coefficient is expected to change with the addition of peroxide. Therefore, Stowers 2008 discloses a “coating material compris[ing] metal ions with radiation sensitive ligands.”

101. Moreover, as shown below, the precursor solutions of Stowers 2008 contain the same components, i.e., HfOCl_2 or ZrOCl_2 , H_2O_2 , and H_2SO_4 , as the precursor solutions used to make the coating materials in the Examples of the '564 patent.

102. As noted above, Example 1 of the '564 patent discloses that “[s]eparate aqueous solutions were prepared for the components of the precursor solution” and “the respective solutions can be referred to as Part A for the metal suboxide cations, Part B for the peroxide-based ligand solution and Part C for the solution comprising polyatomic anions.” *Id.* at 21:18-23. Solution “Part A1” contains “ $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$,” solution “Part A2” contains “ $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$,” solution “Part B” contains “ $\text{H}_2\text{O}_2(\text{aq})$ ”

and solution “Part C” contains “H₂SO₄(aq).” *Id.* at 21:22-55. Example 1 also explains that:

The components in the bottles were then combined by pouring Part A1 or Part A2 component solution into Part B component solution, waiting 5 minutes, then pouring Part C into the combined Part A1 or Part A2 and Part B and waiting another 5 minutes.

Id. at 21:51-56.

103. Finally, “a 30 mL formulation of Zr based precursor solution with a final zirconium concentration of 0.16 M was obtained by combining 4.8 mL of solution Part A1 [ZrOCl₂], 1.8 mL of solution Part B (H₂O₂), 2.16 mL of solution Part C (H₂SO₄(aq)), and 21.24 mL of ultrapure water.” *Id.* at 21:57-62. Likewise, “a 30 mL formulation of an Hf based precursor solution with a final hafnium concentration of 0.15 M was obtained by combining 4.5 mL of solution Part A2 [HfOCl₂], 16.875 mL of solution Part B (H₂O₂), 1.8 mL of solution Part C (H₂SO₄(aq)), and 6.825 mL of ultrapure water.” *Id.* at 21:63-67. Thus, the precursor solutions in Stowers 2008 and the ’564 patent contain the same components, i.e., HfOCl₂ or ZrOCl₂, H₂O₂, and H₂SO₄, and as a result, the resulting coating materials will also contain the same components.

104. Accordingly, although Stowers 2008 does not explicitly state that the resulting “coating material comprises metal ions with radiation sensitive ligands,” this limitation is present in Stowers 2008, because the films of Stowers 2008 contain the same components as the ’564 patent films, and the ’564 patent itself states that the “coating material comprises metal suboxide cations, ligands comprising a peroxide group...” EX1001 at 2:40-43; 22:35-37 (“The coating material was produced according to the method of Example 2 with a ZrO^{+2} -based coating composition.”); 22:61-63 (“The coating material was produced and deposited according to the method of Example 2 with an HfO^{+2} -based coating composition.”).

3. wherein the coating material has an average thickness from 5 nm to 30 nm

105. As noted above, Stowers 2008 states that precursor solutions were spin coated at 3000 rpm for 30 seconds resulting in films 30 to 35-nm thick.” EX1008 at 52. Stowers 2008 also expressly refers to “films on the order of 30-nm thick.” *Id.*, 55; *see also* EX1009 at 265 (Inpria admitting that “Stowers described coatings with thicknesses from 30 to 35 nm in Chapter 3.”). In other words, Stowers 2008 does not merely describe a range of possible thicknesses from 30 nm to 35 nm, but rather, it expressly discloses films with thicknesses from 30 nm to 35 nm, including films that were actually 30 nm thick. Therefore, Stowers 2008 discloses this limitation because

it discloses 30 nm thick HafSOx and ZircSOx films, which is within the claimed thickness range of from 5 nm to 30 nm.

106. To the extent Inpria argues that Stowers 2008 only discloses a general thickness range, I understand that Stowers 2008 can still anticipate. I have been informed that a prior art reference that discloses an overlapping but different range than the claimed range is anticipatory, even where the prior art range only partially or slightly overlaps with the claimed range. To overcome anticipation, Inpria would have to show that the claimed range is somehow critical to the claimed invention. I am not aware of any evidence in the specification or prosecution history that the claimed thickness from 5 nm to 30 nm is critical. In fact, as noted above, the specification does not even disclose that range, so it clearly is not critical to the operability of the claimed invention.

107. Moreover, Example 3 of the '564 patent discloses films that were 10-50 nm thick (clearly an overlapping but different thickness range), yet, Figure 10 in Example 3, shows that “highly resolved patterns were produced ... at a dose level of 20 mJ/cm²” 193 nm UV. This is further evidence that the claimed range of 5 nm to 30 nm is not critical.

4. wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material

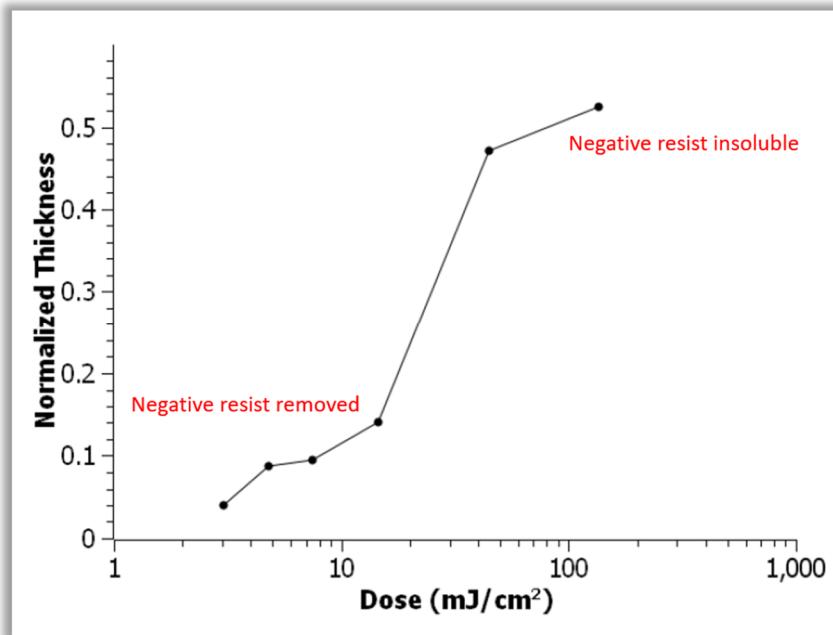
108. Stowers 2008 discloses “[p]atterning by UV light was achieved by exposing films through a chrome-on-silica mask” and that ZircSO_x could be patterned by UV light in either positive or negative tone.” *Id.* at 68-70. Stowers 2008 explains that:

Under different processing conditions the photoactive element of the resist is either increasing or decreasing the solubility of the exposed region relative to the unexposed region. To pattern in negative tone, the exposure has to make the film more resistant to dissolution than the unexposed region. Conversely, to pattern in the positive tone the exposure has to make the film less resistant to dissolution than the unexposed region.

Id. at 70-72. In other words, Stowers 2008 discloses that exposure of a ZircSO_x film to UV radiation altered the chemical properties of the film such that the exposed regions have a different dissolution rate than the un-exposed regions of the film.

109. Stowers 2008 also evaluated whether HafSO_x films could be patterned by EUV. Although these “experiments were hampered by an error in processing”

(EX1008 at 73), “a contrast of 0.3 and a sensitivity of 194 mJ/cm² [d_{0.8}] were demonstrated.” *Id.* Fig. 3-6 of Stowers 2008 shows a “Characteristic [negative resist] contrast curve for EUV exposed HafSOx.”



EX1008 at 79 (with red annotations added).³

110. The contrast curve above shows that as the EUV dose increases, the HafSOx coating becomes more insoluble to the developer. This contrast curve indicates that exposure to EUV altered the chemical properties of the film such that the exposed regions have a different dissolution rate than the un-exposed regions of

³ A contrast curve describes the remaining resist thickness after development of a uniformly illuminated resist film versus the logarithm of the applied exposure dose.

the film. *See also* Fig. 3-7 (showing “SEM image of 30 nm lines and spaces patterned by EUV interference lithography.”) That HafSOx films could be patterned by EUV indicates that exposure to EUV altered the chemical properties of the film such that the exposed regions have a different dissolution rate than the un-exposed regions of the film.

B. Claim 2; The structure of claim 1 wherein the metal ions comprise metal suboxide ions

111. As discussed above with respect to claim 1, the films of Stowers 2008 include ZrO^{2+} or HfO^{2+} cations, which are metal suboxide ions, as confirmed by the named inventors’ own assertion in the ’564 patent itself. EX1001 at 10:45-59 (“Metal suboxide cations of particular interest include, for example, ZrO^{2+} ..., [or] HfO^{2+} ...”); EX1021 ¶0009 (“hafnium suboxide (HfO^{2+}), may be provided by providing an aqueous solution of hafnium oxy chloride ($\text{HfOCl}_2(\text{aq})$).”). Stowers 2008 therefore discloses this limitation.

C. Claim 3: The structure of claim 1 wherein the metal of the metal ions comprises ...Zr, ...Hf, ...

112. As discussed above with respect to claim 1, the films of Stowers 2008 include ZrO^{2+} or HfO^{2+} cations, in which the metal is Zr or Hf. Stowers 2008 therefore discloses this limitation.

D. Claim 4: The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands

113. As discussed above with respect to claim 1, the films of Stowers 2008 include peroxide. Stowers 2008 therefore discloses this limitation.

E. Claim 5: The structure of claim 1 wherein the coating material further comprises polyatomic anions

114. Stowers 2008 discloses adding H_2SO_4 to the working precursor solutions. EX1008 at 52 (“ H_2SO_4 (aq) was added to give a metal to sulfate ratio of 1 to 0.5-0.7.”). H_2SO_4 exists in solution as SO_4^{2-} , *i.e.*, a polyatomic anion. EX1021 ¶0009 (“polyatomic anion in solution, such as sulfate (SO_4^{2-}), may be provided by providing an aqueous solution of sulfuric acid ($\text{H}_2\text{SO}_4(\text{aq})$)”); *see also* EX1001 at 11:48-20 (“Suitable oxygen-based polyatomic anions include, for example, SO_4^{2-} ...”). Stowers 2008 therefore discloses this limitation.

F. Claim 7: The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists

115. As I explained above, the HfSOx films of Stowers 2008 contain the same components as the HfSOx films exemplified in the '564 patent, *i.e.*, they are made using precursor solutions that include HfOCl_2 , H_2O_2 , and H_2SO_4 .

116. The HfSOx films of Stowers 2008 also have the same Hf ion to peroxide ratio as the HfSOx films exemplified in the '564 patent. Specifically, as

discussed, the ratio of Hf ion to peroxide in Stowers 2008 is 1 Hf to 0.75 peroxide. EX1008 at 52. As explained below with respect to claim 8, the ratio of Hf ion to peroxide saturates at 1 Hf:0.5 peroxide. Therefore, even though the precursor solutions of Stowers 2008 contains 0.75 peroxide per Hf ion, the ratio saturates 0.5 peroxide to 1 Hf. Similarly, even though the ratio of peroxide to Hf ion in the HafSOx precursor solution exemplified in the '564 patent is 6.25 – 8.33, the ratio saturates at 0.5 peroxide to 1 Hf. Therefore, the HafSOx precursor solutions of Stowers 2008 and the '564 patent are therefore the same in all material respects. It therefore follows that the resulting films are also the same.

117. Given this, the HafSOx films of Stowers 2008 necessarily have a “high absorption of EUV radiation relative to conventional radiation-based resists,” as confirmed by the named inventors’ own assertion in the '564 patent itself. EX1001, 8:67-9:2 (“Relative to organic resists, the inorganic coating material provides distinct advantages with respect to absorption of selected radiation...”); 11:26-27 (“HfO²⁺ provides good absorption of electron beam material and extreme UV radiation.”). Stowers 2008 therefore discloses this limitation.

G. Claim 8: The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2

118. A metal ion to radiation sensitive ligand ratio of at least 2 means that there are at least 2 metal ions per radiation sensitive ligands, or at least 1 metal ion per 0.5 radiation sensitive ligand. In other words, the claim requires no more than 0.5 radiation sensitive ligand per metal ion.

119. Stowers 2008 discloses precursor solutions having a Zr or Hf ion to peroxide ligand ratio of 1:0.75, which means that there are 0.75 peroxide ligands per Zr or Hf ion. This peroxide content is greater than the no more than 0.5 radiation sensitive ligand per metal ion recited in the claims. But, as publications from named inventor Douglas Keszler's laboratory show, "[e]ven with excess peroxide in the precursor solution, the Hf:O₂²⁻ ratio saturates near 2:1 in the solution, and it persists in the film." EX1016 at 5; EX1018 at 140 ("the amount of peroxide in the films saturates at less than one peroxide group per hafnium ion"); EX1019 at 5 ("films made with at least a 0.5 peroxide to hafnium ratio behave similarly with respect to oxide network formation, confirming that peroxide content in the films does not exceed ≈ 0.5 per hafnium ion."); *id.* at 4 ("HafSOx films in the exposure-ready condition may be visualized as a matrix of Hf cations, where peroxide is uniformly distributed on a subnanometer scale at a ratio of 1 peroxide per 2 hafnium ions."). In

other words, even when there is more than 0.5 peroxide per metal ion in the precursor solution, the ratio saturates at 0.5 peroxide per metal ion and that ratio persists in the films.

120. Thus, even though the precursor solutions of Stowers 2008 contain more than 0.5 peroxide per Hf or Zr ion, the resulting films contain an Hf or Zr to peroxide ratio of approximately 1:0.5, which is “at least 2.” Stowers 2008 therefore discloses this limitation.

H. Claim 9: The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C to 150° C

121. Stowers 2008 discloses that “[p]ositive tone patterning could be achieved by subjecting the resist to a prebake of 100° C for two min.” EX1008 at 70; 6 (explaining that prebake removes remaining solvent after spin coating and prior to radiation exposure). Stowers 2008 therefore discloses this limitation.

I. Claim 10: The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent

122. A POSA would understand claim 10 to recite a negative tone resist. As the '564 patent explains:

The patterning of the resist generally involves several steps including exposing the resist to a selected energy source, such as through a mask, to record a latent image and then developing and removing selected regions of the

resist. For a positive-tone resist, the exposed regions are transformed to make such regions selectively removable, while for negative-tone resist, the unexposed regions are more readily removable.

EX1001 at 1:53-60; EX1023 ¶0037 (“In the negative patterning, exposure to radiation converts the irradiated coating material into a material that is more resistant to removal with a developer composition relative to the non-irradiated coating material.”) Stowers 2008 discloses developing the films “by immersion in .05-1 M HCl” (EX1008 at 52), which is undisputedly an aqueous solution (*id.* at 72), and states that with HCl, “ZircSOx could be patterned by UV light in either positive or negative tone” (*id.* at 54). Stowers 2008 therefore discloses this limitation.

J. Claim 12: The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²

123. As explained above, the ZircSOx and HafSOx films of Stowers 2008 are the same HafSOx films exemplified in the '564 patent, i.e., they have the same components (HfOCl₂ or ZrOCl₂, H₂O₂, and H₂SO₄) and have the same metal to peroxide ratio (as it saturates to 0.5 peroxide to 1 metal). As confirmed by the named inventors' own assertion in the '564 patent, HafSOx films can be patterned by EUV at a dose of 80 mJ/cm². EX1001 at 23:33-41 (“The EUV images were obtained using projection lithography...After exposure at approximately 80 mJ/cm², a post-

exposure bake of 75 °C. was used prior to development in 25% TMAH. The developed patterns...have pitches of A) 32-nm, B) 30-nm, C) 28-nm and D) 26-nm.”); *see also* EX1022 at 5 (HafSOx film patterned with EUV dose of 70 mJ/cm²). As also confirmed by the named inventors’ own assertion in the ’564 patent, ZircSOx films can be patterned by UV at a dose of 20 mJ/cm². EX1001 at 22:50-54 (“FIG. 10 is a pattern of 120 -nm pitch lines (approximately 60 nm lines and spaces) in a Zr-based coating material produced by 193-nm lithography at a dose level of 20 mJ/cm².”)

124. Thus, like the ZircSOx and HafSOx films of the ’564 patent, the ZircSOx and HafSOx films of Stowers 2008 necessarily “can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²” because they are the same films composed of the same components.

XI. GROUND 3: CLAIMS 1-10 AND 12 ARE OBVIOUS OVER STOWERS 2008

125. Even if the claims are entitled to claim priority to June 1, 2010—which again, I do not believe they should be able to—claims 1-10 and 12 are rendered obvious by Stowers 2008.

A. Independent Claim 1

126. As discussed above, Stowers 2008 teaches HafSOx and ZircSOx films having thicknesses ranging from 30 nm to 35 nm, and this disclosure anticipates

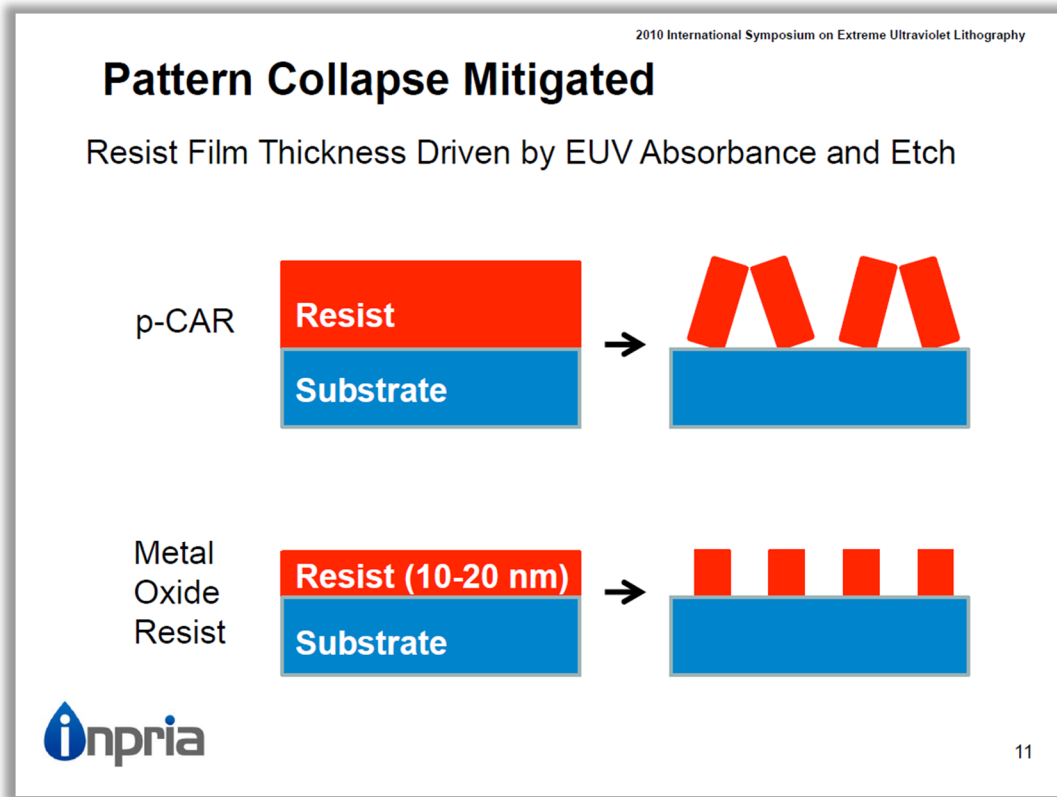
claim 1. To the extent Inpria argues that Stowers 2008 does not anticipate because it does not disclose the claimed thickness range of from 5 nm to 30 nm, Stowers 2008 still renders claim 1 obvious.

127. I have been informed that a prior art reference that discloses an overlapping but different range than the claimed range presumptively renders the claimed range obvious and that the patentee may rebut that presumption by showing that the claimed range produces unexpected results and is therefore critical to the claimed invention.

128. As already discussed above, I am not aware of any evidence in the specification or prosecution history that the claimed thickness from 5 nm to 30 nm is critical. In fact, as noted above, the specification does not even disclose that range, so it clearly is not critical to the operability of the claimed invention. Moreover, in Example 3, “the coating material was deposited at a thickness from 10-50 nm” (EX1001 at 22:7-8), yet “highly resolved patterns were produced...by 193-nm lithography at a dose level of 20 mJ/cm² (which is far less than the maximum dose recited in claim 12). *Id.* at 22:49-51. The failure to even mention the claimed range and the recitation large ranges described in the specification are evidence of a lack of criticality for the claimed “5 nm to 30 nm” thickness.

129. Moreover, a POSA would have recognized that film thickness is a variable that a POSA would have been motivated to optimize. For example, A POSA would have known that pattern collapse, which refers to the deformation of photoresist lines that occurs during the development process, was an issue that needed to be mitigated. *See, e.g.*, EX1012 at Abstract (“However for sub 100 nm line width patterns, the pattern collapse, generated during the drying step of the developing process, becomes a serious limiting phenomenon.”). A POSA would have recognized that film thickness was one parameter that could be optimized to help avoid pattern collapse. *Id.* at 1 (“Two solutions allow avoiding pattern collapse: decreasing the resist thickness or change the dry process step.”); *id.* at 8 (“we have shown that the mode of pattern collapse depends on the pattern height”).

130. Indeed, this was a problem that the named inventors themselves recognized. For example, in a 2010 paper, named inventors Stowers and Keszler stated that “[t]o take advantage of the high etch resistance and to mitigate pattern collapse, the films are targeted for a thickness of approximately 30 nm.” EX1014 at 3. Similarly, in a 2010 presentation, named inventor Stowers stated that pattern collapse was mitigated with resist films that were 10-20 nm thin:



EX1013 at 11; *see also* EX1001 at 18:64-19:6 (“Pattern collapse can be associated with mechanical instability of a high aspect ratio structure such that forces, e.g., surface tension, associated with the processing steps distort the structural elements. Low aspect ratio structures are more stable with respect to potential distorting forces. With the patternable inorganic materials described herein, due to the ability to process effectively the structures with thinner layers of coating material, improved patterning can be accomplished without the need for high aspect ratio patterned coating material.”).

131. Given the ease with which film thickness can be varied, *e.g.*, by adjusting spin rates and times (EX1008 at 6; EX1001 at 14:30-32), finding an optimum thickness range to mitigate pattern collapse would have required nothing more than routine experimentation. Indeed, Stowers 2008 already teaches that depositing films “at 3000 rpm for 30 seconds result[ed] in films 30 to 35-nm thick.” EX1008 at 70; *see also id.* at 86 (“HafSOx has been deposited as thin as 2-3 nm in a film.”). Named inventor Stowers also stated in a 2010 paper that when solutions are “spin coated onto silicon substrates at 3000 rpm for 30 s. ...The resulting film thickness from this procedure was typically 30 nm as measured by ellipsometry.” EX1014 at 2. Thus, a POSA could have easily deposited the claimed coatings at a thickness of 30 nm based on the teachings of Stowers 2008 with routine experimentation.

B. Claim 6: The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm

132. This claim is also rendered obvious by Stowers 2008. Stowers 2008 discloses that “HafSOx, and its zirconium analog ZircSOX, can be deposited in films ranging in thickness from 2 to 500 nm.” EX1008 at 2. Stowers 2008 also states that “HafSOx, a hafnium oxide sulfate, and its zirconium analog ZircSOx are spin-coated materials that exhibit extraordinary film qualities. These materials has (sic) been

deposited in thickness ranges of 3 to 500 nm.” *Id.* at 66; 68 (HafSO_x and ZircSO_x “[f]ilms have been demonstrated as thin as 3 nm with retention of film quality.”); 70 (“HafSO_x has been deposited as thin as 2-3 nm in a film... This serves to demonstrate a fundamental difference of SO_x materials from traditional polymer resists.”)

133. Stowers 2008 thus discloses HafSO_x and ZircSO_x films having thicknesses that overlap with the claimed range of “from 5 nm to 25 nm.” As already discussed above, I am not aware of any evidence of criticality that could rebut this presumption. Moreover, it would have been well within the skillset of a POSA to experiment with the spin rate and time to obtain a thickness of from 5 nm to 25 nm as claimed. EX1008 at 22 (“The spin rates and times must be optimized to provide the desired film thickness.”)

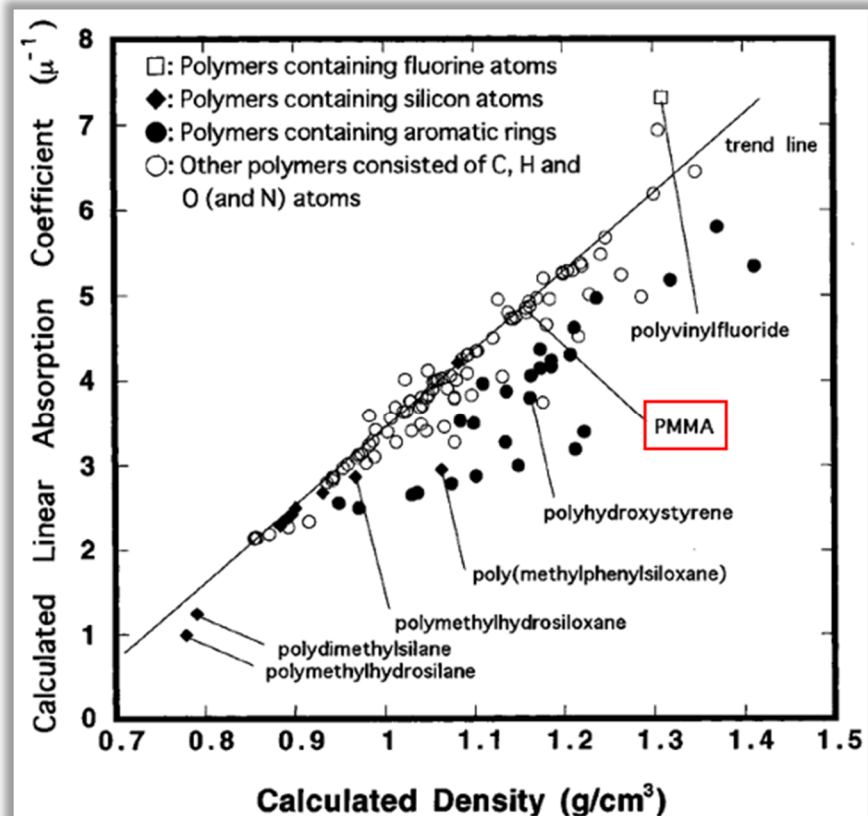
C. Claims 2-5: The structure of claim 1 wherein (i) the metal ions comprise metal suboxide ions (claim 2); (ii) metal of the metal ions comprises ...Zr, ...Hf, (claim 3); (iii) radiation sensitive ligands comprise peroxide ligands (claim 4); (iv) the coating material further comprises polyatomic anions (claim 5)

134. As discussed above with respect to claim 1 in Ground 3, Stowers 2008 discloses each of these limitations.

D. Claim 7: The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists

135. As discussed above, a material's ability to absorb of EUV radiation is an inherent property of the material itself. Thus, because the HafSOx films of Stowers 2008 are the same as the HafSOx films exemplified in the '564 patent in all material respects, the films of Stowers 2008 necessarily have a high absorption of EUV radiation relative to conventional radiation-based resists.

136. To the extent Inpria disputes that the limitation of claim 7 is an inherent property of the HafSOx films of Stowers 2008, this limitation would have been obvious to a POSA. Stowers 2008 discloses that "ZircSOx and particularly HafSOx have a higher density than other resists like HSQ (1.4 g/cm³) or PMMA (1.19 g/cm³)" and points out their "assumed" densities of "4 g/cm² for ZircSOx and 5 g/cm³ for HafSOx." EX1008 at 90. A POSA would have known that as the density increases, the EUV absorbance increases. Indeed, the trend is generally liner, with the EUV absorption coefficient becoming larger as the density increases, as shown in below:



EX1025 at Figure 3 (Y axis shows calculated absorption coefficient at 13 nm, i.e., EUV).

137. Based on this trend, a POSA would have known that ZircSO_x and HafSO_x films have a high absorption of EUV relative to PMMA (polymethyl

methacrylate, i.e., an organic resist) because ZircSOx and HafSOx films have a higher assumed mass density than PMMA. EX1008 at 90.⁴

138. Indeed, this is similar to what named inventor Stowers did in a 2011 publication. Specifically, Stowers explained that “[f]or the current generation of Inpria’s EUV resists, we have selected hafnium as the metal because of its high EUV absorption cross section relative to many other metals.” EX1022 at 3. Stowers further explained that:

We have directly measured the electron density of these materials with X-Ray Reflectivity (XRR). This measurement is combined with compositional information from Electron Probe Micro Analysis (EPMA) to calculate a mass density of 4.7 g/cm³. This mass density and the compositional information are used to calculate EUV absorption from the Center for X-Ray Optics database, which yields an absorption coefficient of 16 μm^{-1} . For comparison, conventional polyhydroxystyrene (PHS) CARs have an EUV absorption coefficient of approximately 4 μm^{-1} , so the MSOx materials are ~4X

⁴ The specification does not define “conventional radiation-based resist.” However, a POSA would have understood that PMMA is a conventional polymer resist. *See, e.g.*, EX1008 at 83 (referring to PMMA as a “traditional polymer” resist).

more absorptive (see Table 1). This absorption enables the use of relatively thin films and efficient capture of a significant fraction of incident EUV photons.

Id.

139. Thus, to the extent Inpria argues that the limitation of claim 7 is somehow not inherent to the claimed material, a POSA would have known that HafSO_x and ZircSO_x are more absorptive of EUV radiation than conventional resists materials, like PMMA, because the POSA would have known that HafSO_x and ZircSO_x have higher mass densities than PMMA, and would have known that as the density increases, so does the EUV absorbance.

E. Claim 8: The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2

140. As explained above, although Stowers 2008 discloses a ratio of metal ion to peroxide ligand of less than 2, i.e., 1 metal to 0.75 peroxide ligand, the ratio saturates at 1 metal to 0.5 peroxide (i.e., 2 metal to peroxide) in solution and that ratio persists in the films. *See, e.g.*, EX1016 at 5.

F. Claim 9: The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C to 150° C

141. As discussed above, Stowers 2008 discloses that “[p]ositive tone patterning could be achieved by subjecting the resist to a prebake of 100° C for two

min.” EX1008 at 70; 6 (explaining that prebake removes remaining solvent after spin coating and prior to radiation exposure).

G. Claim 10: The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent

142. As noted above, a POSA would understand claim 10 to recite a negative tone resist. Stowers 2008 discloses developing the films “by immersion in .05-1 M HCl” (EX1008 at 68), which is undisputedly an aqueous solution (*id.* at 88 (referring to “6-12 M HCl (aq),” i.e., aqueous), and states that with HCl, “ZircSO_x could be patterned by UV light in either positive or negative tone” (*id.* at 70).

H. Claim 12: The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²

143. As discussed above, because the ZircSO_x and HafSO_x films of Stowers 2008 are the same as the ZircSO_x and HafSO_x films exemplified in the '564 patent in all material respects, the films of Stowers 2008 necessarily can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm².

144. To the extent Inpria argues that the ZircSO_x and HafSO_x films of Stowers 2008 do not necessarily satisfy this limitation, a POSA would have reasonably expected that Stowers 2008's ZircSO_x films could be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm².

145. Stowers 2008 discloses that “ZircSOx films were exposed to determine the highest resolution obtainable with our 30 keV electron beam lithography system” and “observed that 16 nm wide isolated features can be patterned at a dose of 112 $\mu\text{C}/\text{cm}^2$.” *Id.* at 89. As named inventor Stowers confirmed in a subsequent publication, an e-beam dose of 249 $\mu\text{C}/\text{cm}^2$ for MSOx films has been “well characterized to correspond to an EUV dose of 25 mJ/cm^2 .” EX1022 at 7. Thus, if an e-beam dose of 249 $\mu\text{C}/\text{cm}^2$ corresponds to an EUV dose of 25 mJ/cm^2 , then it would be reasonable for a POSA to assume that an e-beam dose of 112 $\mu\text{C}/\text{cm}^2$ (which Stowers 2008 states can effectively pattern ZircSOx films) corresponds to a dose of less than 25 mJ/cm^2 , which is “no more than 100 mJ/cm^2 .”

146. Given that Stowers 2008 discloses effective patterning of ZircSOx films with an e-beam dose, which according to Stowers 2011, would necessarily correspond to an EUV equivalent dose of less than 25 mJ/cm^2 , a POSA would reasonably expect that those same ZircSOx films “can be effectively patterned with ... EUV radiation at a dose of no more than 100 mJ/cm^2 ,” especially given that Stowers 2008 states that “resists that function well for electron beam lithography are often good candidates for EUV lithography.” EX1008 at 31.

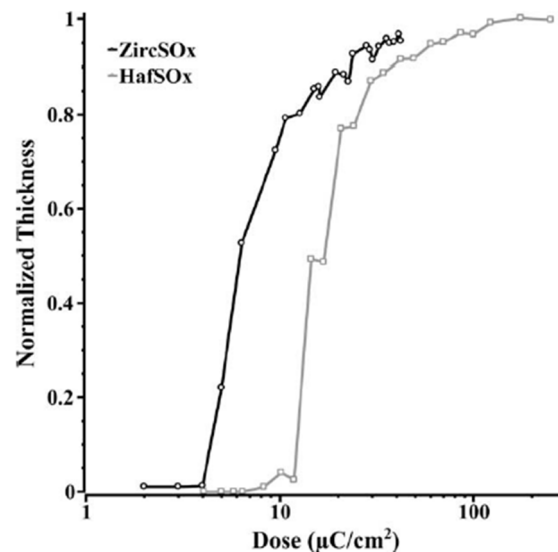
XII. GROUND 4: CLAIM 8 IS OBVIOUS OVER STOWERS 2008 AND STOWERS 2009

147. Claim 8 depends on claim 1 and further states that the claimed structure has “metal ion to radiosensitive ligand ratio of at least 2.” As noted above, Stowers 2008 discloses this limitation because it discloses ZircSO_x and HafSO_x films having a metal to peroxide ratio of 1:0.75, which saturates to a ratio of approximately of 1 metal to 0.5 peroxide (i.e., ratio of 2) in the films, as demonstrated by named inventor Keszler’s own publications. *See, e.g.*, EX1016 at 5.

148. To the extent Inpria argues that the publication of named inventor Keszler should not be believed, this limitation is disclosed in Stowers 2009. Specifically, Stowers 2009 discloses that “[s]olutions for spin coating were prepared by combining the ZrOCl₂ (aq) or HfOCl₂ (aq) with the remaining reagents to produce metal-to-peroxide ratios of 1:0.5.” EX1010 at 19. This ratio is a “metal ion to radiosensitive ligand ratio of at least 2.” A POSA would have been motivated to combine Stowers 2008 and Stowers 2009 because the two prior art references are by the named inventors and relate to the same subject matter as the ’564 patent, i.e., MSO_x films for EUV, UV and e-beam lithography. Moreover, during prosecution of the ’610 patent, Inpria stated that “Stowers [2008] Chapter 2 overlaps

significantly with Stowers [2009]” (EX1009 at 264) and that in fact, “Stowers [2009] is basically chapter 2 of the [Stowers 2008] Thesis.”). *Id.* at 263.

149. Thus, a POSA certainly would have been motivated to combine Stowers 2008 and Stowers 2009, and would have done so with a reasonable expectation of success, because the films in Stowers 2008 and Stowers 2009 have the exact same components, and Stowers 2009 shows that exposure to e-beam radiation altered the chemical properties of the films such that the exposed regions have a different dissolution rate than the un-exposed regions of the films, as shown in the contrast curves below:



EX1010 at Figure 1.

XIII. GROUND 5: CLAIMS 1, 3, 6-7, 9 AND 11-12 ARE ANTICIPATED AND/OR RENDERED OBVIOUS BY TRIKERIOTIS 2010

150. Even if the claims are entitled to claim priority to June 1, 2010—which I do not believe they should be able to—claims 1, 3, 6-7, 9 and 11-12 are rendered obvious by Trikeriotis 2010.

A. Independent Claim 1

1. Preamble: A structure comprising a substrate and a coating material on a surface of the substrate

151. Trikeriotis 2010 discloses that “[u]niform thin films can be spin-coated on Si wafers using either aqueous or PGMEA dispersions of the nanoparticles.” EX1024 at 18.

2. wherein the coating material comprises metal ions with radiation sensitive ligands

152. Trikeriotis discloses “an inorganic resist made of hafnium oxide nanoparticles that can be used both for optical (DUV or EUV) and electron beam lithography.” EX1024 at 16. Trikeriotis 2010 discloses that “Hafnium oxide nanoparticles are used as a core to build the inorganic nanocomposite into an imageable photoresist. During the sol-gel processing of nanoparticles, a variety of organic ligands can be used to control the surface chemistry of the final product.” EX1024 at 15. According to Trikeriotis 2010, “[t]he absorption coefficient of the

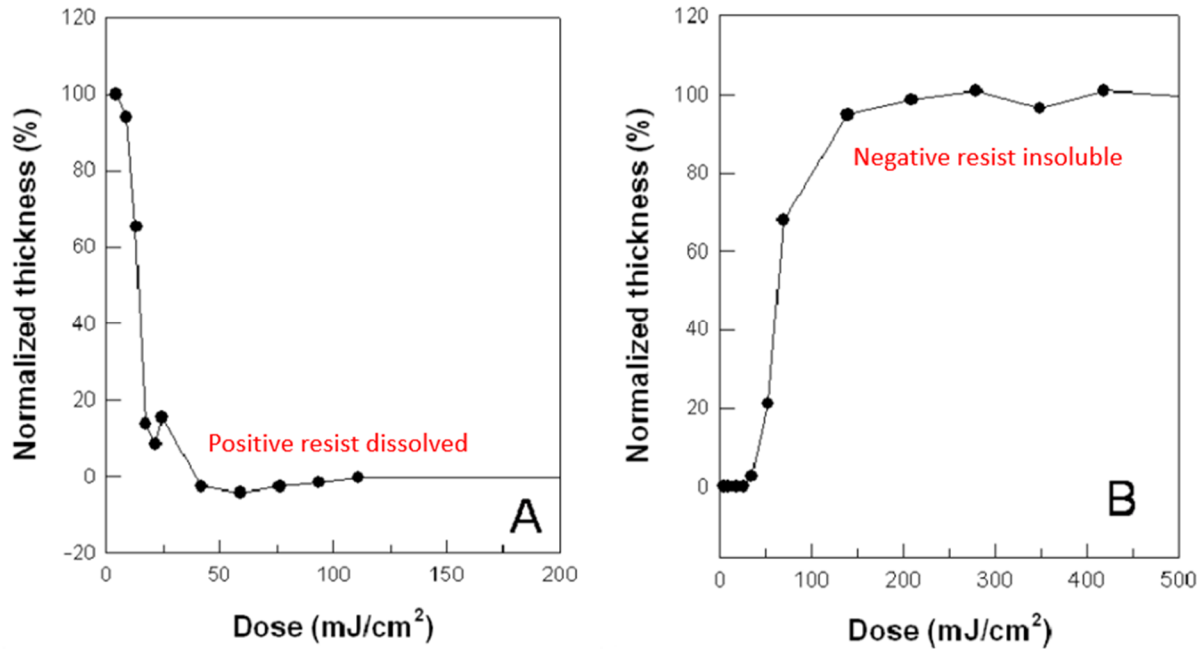
films depends on the ligand...” *Id.* at 18. In other words, the ligands are radiation sensitive.

3. wherein the coating material has an average thickness from 5 nm to 30 nm

153. Trikeriotis 2010 states that “By varying the nanoparticle loading in the dispersion and the spin speed, the film thickness can be controlled...In general, film thicknesses ranging from 30 nm to 200 nm can be easily achieved.” EX1024 at 18. “Figure 8 shows the SEM image of the 60 nm lines and spaces that were printed on the film. The film that was used was only 30 nm thick.” *Id.* at 21.

4. wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material

154. Trikeriotis 2010 states that “To determine the ultimate resolution limits of the nanoparticle photoresist, electron beam lithography was used. Just as in optical lithography, both positive tone and negative tone images could be obtained.” EX1024 at 22. Figure 5 shows contrast curves of the nanoparticle films under 254 nm light exposure:



EX1024 at Figure 5 (red annotations added).

155. These contrast curves demonstrates that the exposure of the films to DUV radiation (254 nm) altered the chemical properties of the films such that the exposed regions have a different dissolution rate than the un-exposed regions of the film.

B. Claim 3: The structure of claim 1 wherein the metal of the metal ions comprises ...Hf ...

156. Trikeriotis 2010 discloses that “Hafnium oxide nanoparticles are used as a core to build the inorganic nanocomposite into an imageable photoresist.”

EX1024 at 15.

C. Claim 6: The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm

157. Trikeriotis 2010 discloses that “Figure 8 shows the SEM image of the 60 nm lines and spaces that were printed on the film. The film that was used was only 30 nm thick.” *Id.* at 21. As explained above, it would have been within the skillset of a POSA to experiment with the spin rate and time to obtain a thickness from 5 nm to about 25 nm, as the ’564 patent itself admits. EX1001 at 14:30-32 (“The spinning speed can be adjusted to obtain a desired coating thickness.”)

D. Claim 7: The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists

158. As discussed above, a POSA would be able to estimate the EUV absorption of any resist material based on its density alone. Trikeriotis 2010’s films are based on hafnium oxide nanoparticles. A POSA would have known that the density of hafnium oxide is approximately 9.68 g/cm³. *See, e.g.*, EX1026 at 4. A POSA would immediately recognize that with a density of 9.68 g/cm³, hafnium oxide necessarily has a higher EUV absorption than conventional organic resist PMMA (approximate density of 1.19 g/cm³) since a POSA would have known that as the mass density increases, the EUV absorption also increases. EX1025 at Figure 3.

E. Claim 9: The structure of claim 1 wherein the coating material has been heated to temperatures from 45° C to 150° C

159. Trikeriotis 2010 states that “Films with the desired thickness are prepared and then baked at 130°C for 60 sec on a hot plate.” EX1024 at 20.

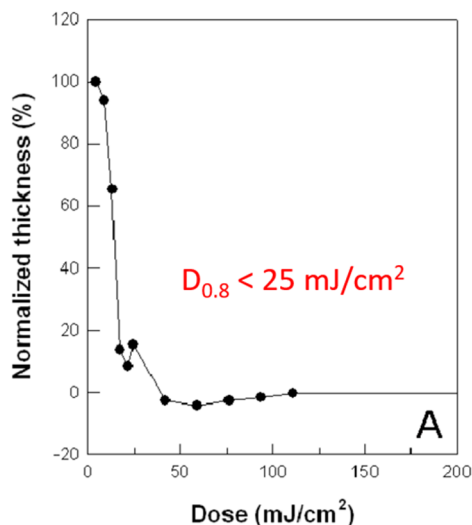
F. Claim 11: The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent

160. A POSA would understand this claim to recite a positive tone image developed in an organic solvent. Trikeriotis 2010 discloses that “[f]or the positive tone imaging, the film is baked after exposure (PEB) at 130°C for 3 min and then aqueous tetrametylammonium hydroxide (TMAH) is used for the development.” EX1024 at 20. TMAH is an organic compound, i.e., it contains carbon. Aqueous TMAH is therefore an “organic” solvent.⁵

G. Claim 12: The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²

161. As shown in Figures 5 and 6 of Trikeriotis 2010, the Hf nanoparticle films can clearly be patterned in positive tone with DUV radiation dose of less than 100 mJ/cm². Specifically, Figure 5A shows a sensitivity of less than 25 mJ/cm² for positive tone resist:

⁵ The '564 patent specification does not define the term “organic solvent.”



EX1024 at Figure 5A (positive tone contrast curve of the nanoparticle films under 254 nm UV light exposure; $D_{0.8}$ sensitivity notation added).⁶

XIV. SECONDARY CONSIDERATIONS

162. I understand that a patent owner may in some circumstances rely on so-called “secondary considerations of non-obviousness” to attempt to refute a finding of obviousness of a claim. I also understand that there are several categories of

⁶ Moreover, as confirmed by Ober, who is an author on Trikeriotis, “[w]e have found that a hafnium oxide (HfO_2) core with a diameter of 2nm, surrounded by organic ligands (binding molecules), can be patterned at EUV wavelengths with extremely high sensitivity ($<5\text{mJ/cm}^2$).” EX1027 at 1-2 (referring to the films of the Trikeriotis reference).

secondary considerations, which might include alleged unexpected results. Notwithstanding that the unpatentability of the challenged claims is supported by strong evidence, it is my opinion that there are no unexpected results that would refute the strong case of obviousness against the challenged claims.

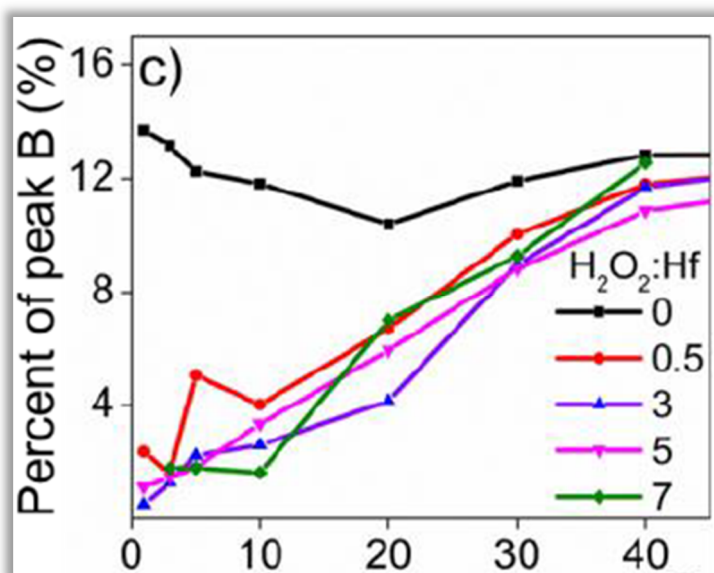
163. For example, I was asked to review Inpria's statement during prosecution of the '872 application. EX1004. There, in an Appeal Brief to the Board, Inpria argued that "the high ligand to metal suboxide cation ratio [of at least 2 recited in the claims] leads to unexpected improvement in the properties of Stowers." EX1004 at 656. However, Inpria did not point to any data, in the specification or elsewhere, that supported this assertion.

164. Moreover, work from named inventor Keszler's laboratory has demonstrated that even with a ratio of peroxide to metal ion of "at least 2" in the precursor solution, the ratio saturates at 0.5 peroxide to metal ion, and that ratio persists in the film. *E.g.*, EX1016 at 5. That work also shows that "[i]ncreasing the amount of peroxide in the solutions above a molar ratio of 0.5 does not cause further changes in the radiation chemistry of the films." EX1018 at 158-160. In a thesis from 2017, one of named inventor Keszler's students wrote that:

Film condensation was also monitored using XPS for films spun from solutions with different amounts of

peroxide (Figure 8.3c). HfSO_x films made without H_2O_2 initially show significant oxide network formation, and no increase is observed with increasing X-ray exposure. Films made with at least a 0.5 peroxide to hafnium ratio in solution show very similar behavior with respect to condensation. This is consistent with results from Raman spectroscopy and wet chemical analysis which indicate that the amount of peroxide in the films saturates at less than one peroxide group per hafnium ion. Increasing the amount of peroxide in the solutions above a molar ratio of 0.5 does not cause further changes in the radiation chemistry of the films.

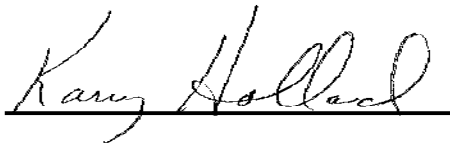
EX1018 at 160. Figure 8.3c is shown below:



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

166. In signing this declaration, I understand that the declaration will be filed as evidence in a contested case before the Patent Trial and Appeal Board of the United States Patent and Trademark Office. I acknowledge that I may be subject to cross examination in the case and that cross examination will take place within the United States. If cross examination is required of me, I will appear for cross examination within the United States during the time allotted for cross examination.

DATE: October 16, 2023

By: 
Karey Holland, Ph.D.