Patent Owner Demonstratives

United States Patent and Trademark Office
Before the Patent Trial and Appeal Board

Lam Research Corp., Petitioner v. Inpria Corp., Patent Owner

U.S. Patent No. 9,823,564

Case: IPR2024-00033

Oral Hearing: January 30, 2025

INPRIA EXHIBIT 2019

Petitioner Has Not Established Any Ground of Unpatentability

Ground 1	Petitioner Fails to Show Anticipation by the ’888 Publication for Claims 1-12
Ground 2	Petitioner Fails to Show Anticipation Over Stowers 2008 for Claims 1-5, 7-10, and 12
Ground 3	Petitioner Fails to Show Obviousness Over Stowers 2008 for Claims 1-10 and 12
Ground 4	Petitioner Fails to Show Obviousness Over Stowers 2008 and Stowers 2009 for Claim 8
Ground 5A/B	Petitioner Fails to Show Anticipation or Obviousness Over Trikeriotis for Claims 1, 3, 6-7, 9, and 11-12
Motion to Amend	Petitioner’s 112, 102, and 103 Arguments Fail

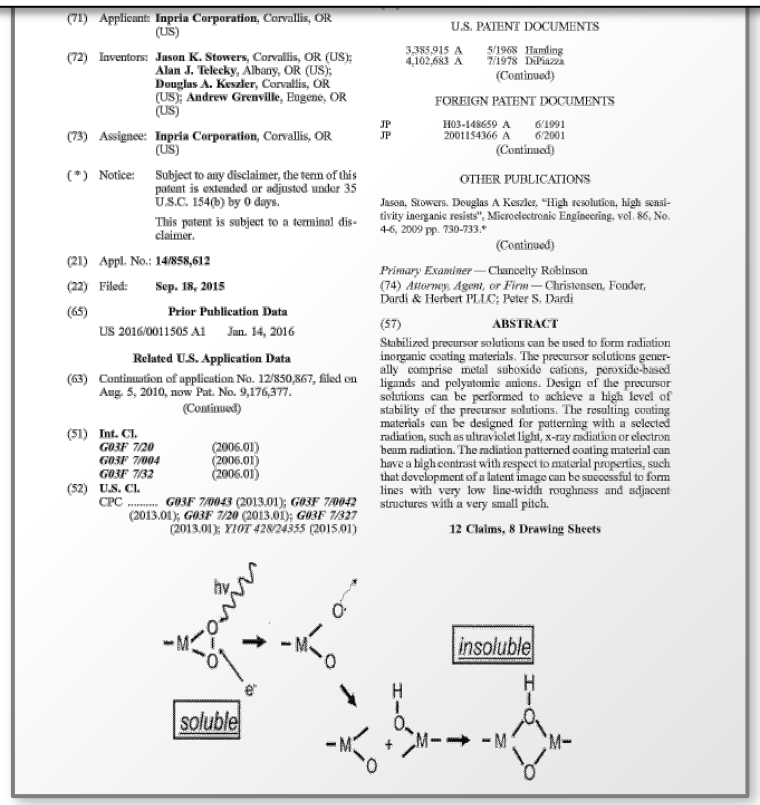
Invention Claimed in the ’564 Patent

(12) **United States Patent**
Stowers et al.

(10) **Patent No.: US 9,823,564 B2**
(45) **Date of Patent: *Nov. 21, 2017**

(54) **PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS**

(58) **Field of Classification Search**
CPC G03F 7/20
See application file for complete search history.



(71) Applicant: **Inpria Corporation**, Corvallis, OR (US)

(72) Inventors: **Jason K. Stowers**, Corvallis, OR (US); **Alan J. Telecky**, Albany, OR (US); **Douglas A. Keszler**, Corvallis, OR (US); **Andrew Grenville**, Eugene, OR (US)

(73) Assignee: **Inpria Corporation**, Corvallis, OR (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/858,612**

(22) Filed: **Sep. 18, 2015**

(65) **Prior Publication Data**

US 2016/0011505 A1 Jan. 14, 2016

Related U.S. Application Data

(63) Continuation of application No. 12/850,867, filed on Aug. 5, 2010, now Pat. No. 9,176,377.
(Continued)

(51) **Int. Cl.**
G03F 7/20 (2006.01)
G03F 7/004 (2006.01)
G03F 7/32 (2006.01)

(52) **U.S. Cl.**
CPC ***G03F 7/0043*** (2013.01); ***G03F 7/0042*** (2013.01); ***G03F 7/20*** (2013.01); ***G03F 7/327*** (2013.01); *Y10T 428/24355* (2015.01)

U.S. PATENT DOCUMENTS

3,385,915 A 5/1968 Harding
4,102,683 A 7/1978 DiPazza
(Continued)

FOREIGN PATENT DOCUMENTS

JP H03-148659 A 6/1991
JP 2001154366 A 6/2001
(Continued)

OTHER PUBLICATIONS

Jason, Stowers. Douglas A Keszler, "High resolution, high sensitivity inorganic resists", Microelectronic Engineering, vol. 86, No. 4-6, 2009 pp. 730-733.*
(Continued)

Primary Examiner — Chanceity Robinson
(74) *Attorney, Agent, or Firm* — Christensen, Fonder, Dardi & Herbert PLLC; Peter S. Dardi

(57) **ABSTRACT**

Stabilized precursor solutions can be used to form radiation inorganic coating materials. The precursor solutions generally comprise metal suboxide cations, peroxide-based ligands and polyatomic anions. Design of the precursor solutions can be performed to achieve a high level of stability of the precursor solutions. The resulting coating materials can be designed for patterning with a selected radiation, such as ultraviolet light, x-ray radiation or electron beam radiation. The radiation patterned coating material can have a high contrast with respect to material properties, such that development of a latent image can be successful to form lines with very low line-width roughness and adjacent structures with a very small pitch.

12 Claims, 8 Drawing Sheets

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.

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

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/cm^2.

EX1001, Claims 1, 6, 7, 12

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Motion to Amend	Petitioner's 112, 102, and 103 Arguments Fail

Petitioner Has Not Established Anticipation by the ’888 Publication

- Written Description Legal Standard
- Specification Provides Sufficient Written Description
  - The ’867 Application Description
  - Sufficient Under Precedent
- Prosecution History
  - Petitioner Provides No Proper Legal Basis for its Theory
  - Petitioner Misconstrues Prosecution Statements

Written Description Legal Standard

- **Written Description Legal Standard**
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Written Description Legal Standard

- **The written description requirement is satisfied when the relied-upon disclosure "reasonably conveys to those skilled in the art that the inventor had possession of the claimed subject matter as of the filing date."**

  Ariad Pharms., Inc. v. Eli Lilly & Co., 598 F.3d 1336, 1351 (Fed. Cir. 2010) (en banc)

- **"The specification need not expressly recite the claimed range to provide written description support.**

  RAI Strategic Holdings, Inc. v. Philip Morris Prods. S.A., 92 F.4th 1085, 1090 (Fed. Cir. 2024)

- **"[T]he level of detail required to satisfy the written description requirement varies depending on the nature and scope of the claims and on the complexity and predictability of the relevant technology."**

  Ariad, 598 F.3d, 1351

- **When predictable claim limitations are at issue "a lower level of detail is required to satisfy the written description requirement than for unpredictable arts."**

  RAI Strategic Holdings, Inc. v. Philip Morris Prods. S.A., 92 F.4th 1085, 1090 (Fed. Cir. 2024)
  (quoting *Hologic, Inc. v. Smith & Nephew, Inc.*, 884 F.3d 1357, 1361 (Fed. Cir. 2018))

- **The test for written description support "requires an objective inquiry into the four corners of the specification from the perspective of a person of ordinary skill in the art."**

  Ariad, 598 F.3d, 1352

The ’867 Application Description

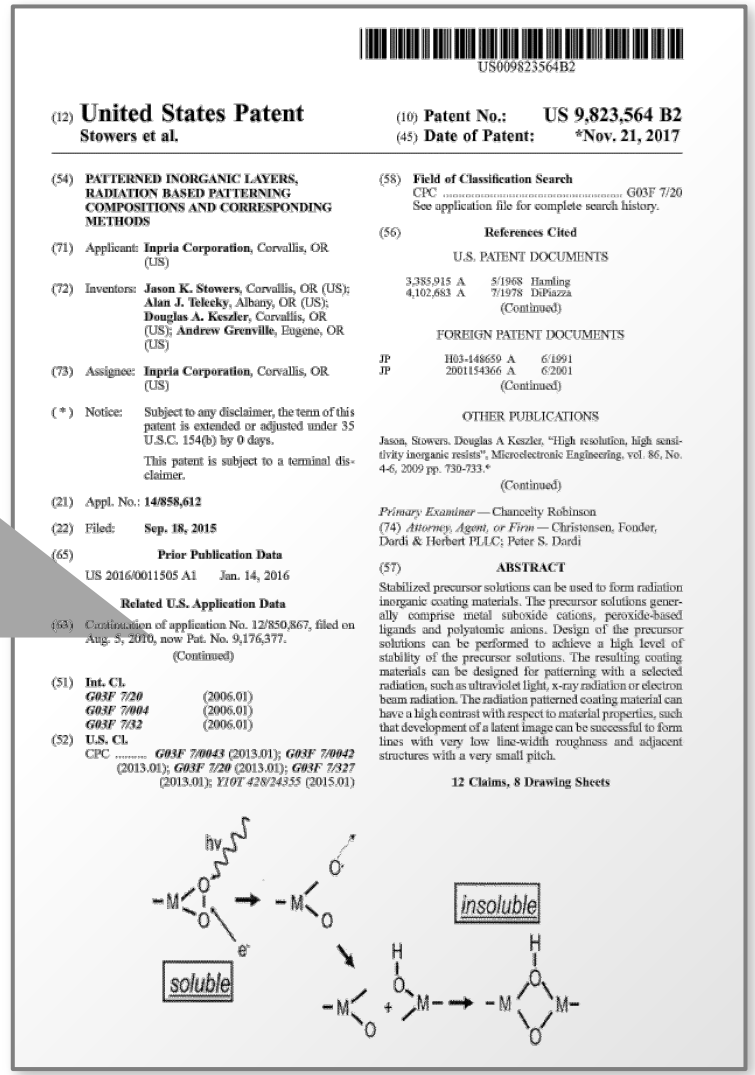
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The ’867 Application Description

- **The ’564 patent was filed as a continuation from the ’867 application.**
- **Same disclosures in both**

Related U.S. Application Data

(63) Continuation of application No. 12/850,867, filed on Aug. 5, 2010, now Pat. No. 9,176,377.



US009823564B2

(12) **United States Patent**
Stowers et al.

(10) **Patent No.: US 9,823,564 B2**
(45) **Date of Patent: *Nov. 21, 2017**

(54) **PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS**

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FOREIGN PATENT DOCUMENTS

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OTHER PUBLICATIONS

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Primary Examiner — Chanceity Robinson
(74) *Attorney, Agent, or Firm* — Christensen, Fonder, Dardi & Herbert PLLC; Peter S. Dardi

(57) **ABSTRACT**

Stabilized precursor solutions can be used to form radiation inorganic coating materials. The precursor solutions generally comprise metal suboxide cations, peroxide-based ligands and polyatomic anions. Design of the precursor solutions can be performed to achieve a high level of stability of the precursor solutions. The resulting coating materials can be designed for patterning with a selected radiation, such as ultraviolet light, x-ray radiation or electron beam radiation. The radiation patterned coating material can have a high contrast with respect to material properties, such that development of a latent image can be successful to form lines with very low line-width roughness and adjacent structures with a very small pitch.

12 Claims, 8 Drawing Sheets

The ’867 Application Description

Specification Discloses Several Exemplary Thicknesses

- From about 1 nm to about 25 nm
- From about 1 nm to about 40 nm
- From about 1 nm to about 50 nm
- No more than about 250 nm
- No more than about 1 micron
- Examples: 10-50 nm; 20 nm

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. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.

EX1001, 14:43-61; EX1004, 23:14-26

Example 3: 193-nm Lithographic Patterning of a Zr Based Coating Material

This example describes a method that has been used to pattern a Zr suboxide based coating material.

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 form 10-50 nm. The Zr-based coating material was irradi-

Example 4: Electron-Beam and EUV Lithographic Patterning of an Hf Based Coating Material

This example describes a method that has been used to pattern an Hf suboxide based coating material.

. . .

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

EX1001, 22:30-23:41; EX1004, 35:10-37:2

The ’867 Application Description

Specification Discloses Several Exemplary Thicknesses

- **“additional ranges of thicknesses within the explicit ranges”**

> 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. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.

EX1001, 14:43-61; EX1004, 23:14-26

The ’867 Application Description

Specification Discloses How to Vary and Measure Thickness

- **The specification describes how the thickness can be varied and explains variables that affect the thickness.**
  - **Concentrations – EX1004, 11:18-20, 21:3-7**
  - **Coating Techniques – EX1004, 12:20-25, 22:21-30**
  - **Spin Speeds – EX1004, 23:1-13**
- **The specification also describes how the thickness can be evaluated to confirm a desired thickness.**

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. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.

EX1001, 14:43-61; EX1004, 23:14-26

POR, 10; Sur-Reply, 2-4

The ’867 Application Description

Petitioner Agrees Changing Thickness Is Predictable

the art.” *Applied Materials*, 692 F.3d at 1295. Given the ease with which film thickness can be varied, *e.g.*, by adjusting spin rates and times (EX1008, 6; EX1001, 14:30-32 (’564 patent admitting as much)), finding an optimum thickness range would have required nothing more than routine experimentation. EX1002 ¶131.

Pet., 50

nm thick.” EX1024, 21. It would have been within the routine skillset of a POSA to experiment with the spin rate and time to obtain the desired thickness. EX1002 ¶157.

Pet., 60

Moreover, there is also no dispute that film thickness is a result-effective variable that a POSA would have found obvious to optimize. *In re Applied Materials, Inc.*, 692 F.3d 1289, 1297 (Fed. Cir. 2012) (“A recognition in the prior art that a property is affected by the variable is sufficient to find the variable result-effective.”) Here, A POSA would have known that pattern collapse, which refers to

Pet., 49

The ’867 Application Description

Dr. Holland Agrees Changing Thickness Is Predictable

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

EX1002, ¶131; *see also* EX1040, ¶132 (same)

13 So here, you're saying that is easy for a
14 person of skill in the art to vary film thicknesses?
15 A. It is, yes, as I understand it with at least
16 the resists I'm used to working with.

EX2011, 175:13-16; *see also id.*, 56:14-57:16

14 Q. So you wouldn't consider achieving a particular
15 thickness to be unpredictable, would you?
16 A. I would think that a person of skill in the art
17 would know how to optimize it. It might take a while,
18 but they would be able to optimize it.

EX2017, 25:14-18

3 Q. It's okay. I'll repeat. So are the viscosity,
4 precursor solution, and spin speed -- these variables
5 describing how to achieve a particular thickness?
6 A. Yes, they do say that. Yes.
7 Q. And this would --
8 (Simultaneous colloquy.)
9 A. -- part of it, yeah.
10 Q. And this would go to how easy or difficult it
11 would be to achieve different thicknesses, right?
12 A. Yes.

EX2017, 26:3-12

Sufficient Under Precedent

- Written Description Legal Standard
- Specification Provides Sufficient Written Description
  - The ’867 Application Description
  - **Sufficient Under Precedent**
- Prosecution History
  - Petitioner Provides No Proper Legal Basis for its Theory
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Sufficient Under Precedent

RAI Strategic Holdings, Inc. v. Philip Morris Prods. S.A., 92 F.4th 1085 (Fed. Cir. 2024)

(emphases added). In addition to considering what the specification expressly discloses, we also consider the context of the technology at issue and the knowledge gained by a person of ordinary skill in the art reading the specification. Given the predictability of electro-mechanical inventions such as the one at issue here, and the lack of complexity of the particular claim limitation at issue—*i.e.*, reciting the length of a heating member—"a lower level of detail is required to satisfy the written description requirement than for unpredictable arts." *See Hologic, Inc. v. Smith & Nephew, Inc.*, 884 F.3d 1357, 1361 (Fed. Cir. 2018). Further, nothing in the specification indicates that changing the length of the heating member changes the invention, whether as to operability, effectiveness, or any other parameter.

RAI, 92 F.4th, 1090

	Claim	Specification
RAI	"about 75% to about 85%"	"about 75% to about 125%" "about 80% to about 120%" "about 85% to about 115%" "about 90% to about 110%"
'564 Patent	"5 nm to 30 nm" "5 nm to 25 nm"	Less than 1000 nm Less than 250 nm About 1 nm to about 50 nm About 1 nm to about 40 nm About 1 nm to about 25 nm "additional ranges of thicknesses within the explicit ranges above"

POR, 22-23

POR, 6-7, 17, 22-23; Sur-Reply, 4, 7

Sufficient Under Precedent

Petitioner Demands Express Disclosure

As these passages make clear, the '867 application does not describe a coating material with a particular thickness of either 5 nm or 30 nm, let alone a thickness **range** of 5 nm to 30 nm (claim 1). While the '867 application does recite a thickness of 25 nm, it never recites a thickness of 5 nm, let alone a thickness **range** of 5 nm to 25 nm (claim 6).[4] There is absolutely no indication in the '867 application that the

Pet., 15

Dr. Holland Demands Express Disclosure

Q. So the specification itself would need to mention those particular end points for a range to have written description support, right?

A. As I understand it, yes.

EX2017, 33:7-10; *see also id.*, 32:14-33:10

But Express Disclosure Not Required

The specification need not expressly recite the claimed range to provide written description support. *See id.* ("[T]he inven-

RAI, 92 F.4th, 1090

Petitioner Provides No Proper Legal Basis for its Theory

- Written Description Legal Standard
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  - The ’867 Application Description
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- **Prosecution History**
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  - Petitioner Misconstrues Prosecution Statements

Petitioner Provides No Proper Legal Basis for its Theory

- **Petition: "estopped" – No authority or basis**

> Moreover, having successfully argued that 30 nm and 35 nm "are not close enough that one would expect them to have the same properties" (EX1007, 508), Inpria should be estopped from now arguing that 5 nm is "close enough" to 1 nm or 10 nm, or that 30 nm is "close enough" to 25 nm, 40 nm, or 50 nm, such that these endpoint values provide support for the claimed ranges of 5 nm to 30 nm (claim 1) or 5 nm to 25 nm (claim 6). *See also* EX1009, 264 ("A person skilled in the art would not understand a 5 nm different (sic) to fall within the scope of about 30 nm."); EX1002 ¶67.

Pet., 17

- **Reply: "public notice function"**
  - ***Teva* – Regarding indefiniteness and claim construction**

> Inpria also confuses issue preclusion, prosecution history estoppel, and the general legal principle of estoppel. POR at 19-22. Lam neither argues "prosecution history estoppel." nor "issue preclusion." POR at 21.
>
> Instead, "[t]he public notice function of a patent and its prosecution history requires that a patentee be held to what he declares during the prosecution of his patent." *Teva Pharms. USA, Inc. v. Sandoz, Inc.*, 789 F.3d 1335, 1344 (Fed. Cir. 2015). And it is irrelevant that patentee's statements were made in the context of an

Reply, 6

POR, 18-20; Sur-Reply, 5

Petitioner Provides No Proper Legal Basis for its Theory

No Disclaimer Under *Bradford*

- **Petitioner Entirely Fails to Explain Theory**
  - **Simply argues "such statements may be highly relevant" and includes this string cite:**

> satisfied. *OrthoAccel Techs., Inc. v. Propel Orthodontics, LLC*, 785 F. App'x 871, 875 (Fed. Cir. 2019) (affirming district court's "reli[ance] on evidence from the prosecution history of the [asserted] patent" to determine written description); *ICN Photonics, Ltd., v. Cynosure, Inc.*, 73 F. App'x 425, 429 (Fed. Cir. 2003); *Bradford Co. v. Conteyor N. Am., Inc.*, 603 F.3d 1262, 1269-70 (Fed. Cir. 2010).

Reply, 6

- **In *Bradford*, "compelling disclaimer" was found because the patentee argued (1) a parent patent did not have a feature to overcome double patenting and (2) the parent patent did have the feature to support written disclosure.**

Bradford Co. v. Conteyor N. Am., Inc., 603 F.3d 1262, 1269-70 (Fed. Cir. 2010)

- **Here, by contrast, Lam argues that Inpria's prosecution arguments distinguishing a different document (Stowers 2009, not the priority '867 application) with a different range and disclosures than in the priority document should "estop" Inpria from claiming priority.**

- **Not a "clear and unambiguous disavowal."**

Storage Tech. Corp. v. Cisco Sys., Inc., 329 F.3d 823, 833 (Fed. Cir. 2003)

Sur-Reply, 5-6

Prosecution History

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Petitioner Misconstrues Prosecution Statements

Prosecution History Comparing Claimed Range to Prior Art

With regard 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. As indicated by the Examiner, Meyers does not teach or suggest a thickness between 5 nm and 30 nm. Stowers in view of Meyers does not teach or suggest each and every element of claim 1. The combination of Stowers and Meyers therefore does not render claim 1 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

EX1007, 508

On page 5 of the Office Action, the Examiner admits that "Stowers do not explicitly recite the thickness or differential dissolution as instantly claimed." The Examiner cites Stowers et al. for teaching the thickness. But respectfully this assertion regarding Stowers et al. is incorrect for two reasons. First, the Examiner asserts that 35 nm is about 30 nm, but reference to Fig. 4 of Stowers et al. and the discussion on page 21 of the present application suggests that the thickness can be evaluated on the order of one nm. A person of ordinary skill in the art would not understand a 5 nm different to fall within the scope of about 30 nm. Second, Stowers et al. use their thickness of patterning coating for performing e-beam patterning. The Examiner asserts that Stowers et al.

EX1009, 264

Petitioner Argues Claimed Range Is Not Critical

Ground 2: Claims 1-5, 7-10, 12 Are Anticipated by Stowers 2008

Petitioner is not aware of any evidence in the specification or prosecution history that the claimed range of "from 5 nm to 30 nm" is critical. In fact, the specification

Pet., 33, 39

POR, 20; Sur-Reply, 6-7

Petitioner Misconstrues Prosecution Statements

Claim 1

between ~~about~~ 5 nm and ~~about~~ 30 nm

35 nm or greater

Stowers 2009

With regard to claim 1, the combination of Stowe[illegible] 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. As indicated by the Examiner, Meyers does not teach or suggest a thickness between 5 nm and 30 nm. Stowers in view of Meyers does not teach or suggest each and every element of claim 1. The combination of Stowers and Meyers therefore does not render claim 1 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

EX1007, 508

POR, 20; Sur-Reply, 6-7

Petitioner Misconstrues Prosecution Statements for Claim 1

Specification Ranges

- From about 1 nm to about 25 nm
- From about 1 nm to about 40 nm
- From about 1 nm to about 50 nm
- No more than about 250 nm
- No more than about 1 micron
- Additional ranges of thicknesses within the explicit ranges
- Examples: 10-50 nm, 20nm

WD compares claim to entire specification

Claim 1

between ~~about~~ 5 nm and ~~about~~ 30 nm

Prosecution history compared claimed thickness to Stowers 2009 thickness

X

35 nm or greater

Stowers 2009

POR, 20; Sur-Reply, 6-7

Petitioner Misconstrues Prosecution Statements for Claim 6

Specification Ranges

- From about 1 nm to about 25 nm
- From about 1 nm to about 40 nm
- From about 1 nm to about 50 nm
- No more than about 250 nm
- No more than about 1 micron
- Additional ranges of thicknesses within the explicit ranges
- Examples: 10-50 nm, 20nm

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

EX1001, Claim 6

between ~~about~~ 5 nm and ~~about~~ 30 nm

X

X

35 nm or greater

Stowers 2009

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Pet., 3; Inst. Dec., 5

Petitioner's Stowers 2008 Arguments Are Deficient

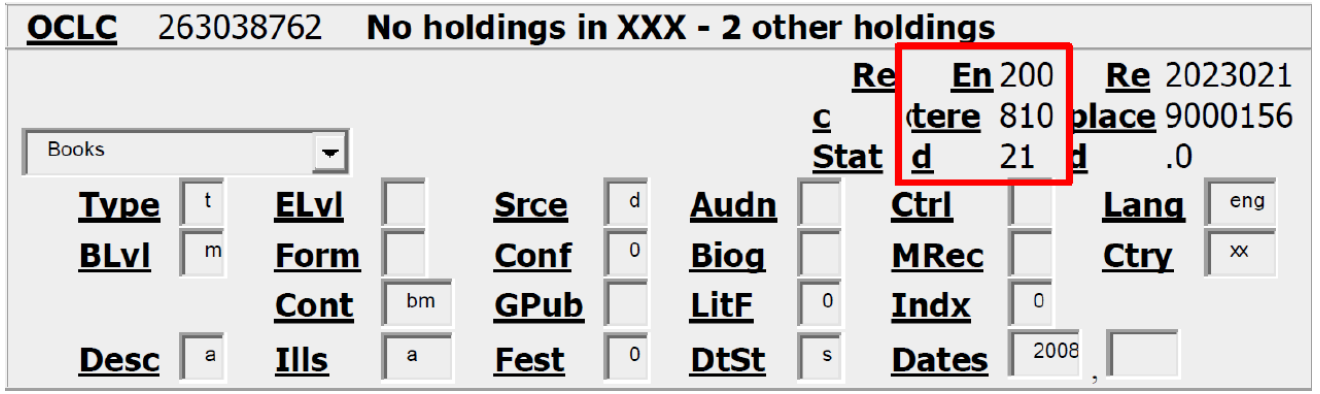
- Stowers 2008 Is Not Prior Art
- Claim 1 – Petitioner's "Same Films" Inherency Theory
- Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient
- Claim 1 – Exposure … Alters the Chemical Properties
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Stowers 2008 Is Not Prior Art

- **Stowers 2008 Is Not Prior Art**
- Claim 1 – Petitioner's "Same Films" Inherency Theory
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Stowers 2008 Is Not Prior Art – Embargo

- **Petition – Lam submitted Dr. Hall-Ellis Declaration**
  - **Dr. Hall-Ellis relied on "entered" field in MARC record:**



OCLC 263038762 No holdings in XXX - 2 other holdings

Books

Type	t	ELvl		Srce	d	Audn		Ctrl		Lang	eng
BLvl	m	Form		Conf	0	Biog		MRec		Ctry	xx
		Cont	bm	GPub		LitF	0	Indx	0		
Desc	a	Ills	a	Fest	0	DtSt	s	Dates	2008		

Entered 20081021

Replaced 20230219000156.0

EX1006, 41

State University. As can be seen in the "Entered" field in the MARC record for this exhibit, a cataloger in The Valley Library at Oregon State University created OCLC record number 263038762 on October 21, 2008, as show in the "Entered" field ("20081021"). The library continues to update and enhance this MARC

EX1006, ¶47

`

Stowers 2008 Is Not Prior Art – Embargo

- **POR – Inpria showed that Stowers 2008 was unavailable prior to critical date due to one year embargo**
  - **Jason Stowers Declaration:**

> 7. When I submitted my thesis in October 2008, I requested that it be embargoed for a period of one year before it would be released to the public. I understood this to mean that my thesis would be unavailable to the public until sometime in October 2009, one year after I submitted it.

EX2008, ¶7

  - **Contemporaneous email:**

> On Feb 23, 2010, at 9:14 PM, Jason Stowers wrote:
>
> FYI,
> My Dissertation is now past its 1 year publication embargo.

EX2008, 6

  - **Embargo functionality handled separately**

> final approver. Publishing creates that Date Available timestamp, though it doesn't necessarily mean it was fully public, just that it had fully completed the approval process. The embargo functionality was handled separately from the approval workflow, and didn't create the same provenance trail.

EX2012, 1

Stowers 2008 Is Not Prior Art – Embargo

- **<u>Reply</u> – Lam never cites Hall-Ellis and instead includes new Engelbert Email and Stewart Declaration**
  - **Engelbert Email**

> I'm not aware of any declaration or certi•cation that we provide for our resources, but the date that the dissertation was published through our archive is coded into the record. OSU Libraries made this dissertation publicly available on 10-21-2008. We would have received it before that date because there is a certain amount of processing and description that is done before it is published in the archive, but there isn't a record of that date. I don't know if that helps. Let me know if you have any other questions.

EX1042, 1

Contradicted by Key Email

> final approver. Publishing creates that Date Available timestamp, though it doesn't necessarily mean it was fully public, just that it had fully completed the approval process. The embargo functionality was handled separately from the approval workflow, and didn't create the same provenance trail.

EX2012, 1

Stowers 2008 Is Not Prior Art – Embargo

- **<u>Reply</u> – Lam never cites Hall-Ellis and instead includes new Engelbert Email and Stewart Declaration**

Original Stewart Declaration

Full Text Availability

First Received by UMI/ProQuest:	12/7/2008
First Made Available for Sale (print or electronic)	01/2009
DAI volume issue:	DAI-B 69/11
DAI publication month and year:	01/2009
Date full text is loaded into PQDT:	01/15/2009
Information available on restrictions:	None

Dissertation Number 3336399 was loaded into PQDT on January 15, 2009, and was therefore fully searchable in PQDT and available as of this date.

EX1041, ¶8

Supplemental Stewart Declaration

Full Text Availability

First Received by UMI/ProQuest:	12/7/2008
First Made Available for Sale (print or electronic)	12/08/2009
DAI volume issue:	DAI-B 69/11
DAI publication month and year:	01/2009
Date full text is loaded into PQDT:	12/08/2009
Information available on restrictions:	Dissertation submitted with 1 year embargo. Embargo start date: 12/07/2008. Embargo end date: 12/07/2009

9. Dissertation Number 3336399 full text was loaded into PQDT on December 8, 2009, and was therefore fully searchable in PQDT and available as of this date.

EX2013, ¶¶8-9

Stowers 2008 Is Not Prior Art – Timeline

Presented August 14, 2008
Commencement June 2009

EX1008, 5

Full Text Availability

First Received by UMI/ProQuest:	12/7/2008
First Made Available for Sale (print or electronic)	12/08/2009

EX2013, ¶8

On Feb 23, 2010, at 9:14 PM, Jason Stowers wrote:

FYI,
My Dissertation is now past its 1 year publication embargo.

EX2008, 6

Dissertation defense

ProQuest Received

ProQuest Made Available

Stowers Email

August 14, 2008	October 21, 2008	December 7, 2008	August 5, 2009	December 8, 2009	February 23, 2010	August 5, 2010

OSU Library Record Entered



EX1006, 41

Pre-AIA 35 U.S.C. § 102(b)
Critical Date

'564 Patent Effective Filing Date

Related U.S. Application Data

(63) Continuation of application No. 12/850,867, filed on Aug. 5, 2010, now Pat. No. 9,176,377.

EX1001, Cover

Claim 1 – Petitioner's "Same Films" Inherency Theory

- Stowers 2008 Is Not Prior Art
- **Claim 1 – Petitioner's "Same Films" Inherency Theory**
- Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient
- Claim 1 – Exposure … Alters the Chemical Properties
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Legal Standard – Inherency

Inherency Has a High Burden of Proof

- **"To serve as an anticipation when the reference is silent about the asserted inherent characteristic, such gap in the reference may be filled with recourse to extrinsic evidence. Such evidence must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill."**

  Cont'l Can Co. USA v. Monsanto Co., 948 F.2d 1264, 1268 (Fed. Cir. 1991)

- **"Inherency, however, may not be established by probabilities or possibilities."**

  In re Oelrich, 666 F.2d 578, 581 (C.C.P.A. 1981)

- **"The inherent result must inevitably result from the disclosed steps."**

  In re Montgomery, 677 F.3d 1375, 1380 (Fed. Cir. 2012)

Petitioner Did Not Prove That the Films Are Identical

Petition Did Not Acknowledge Differences

> There can be no dispute that the precursor solutions in Stowers 2008 and the '564 patent combine the exact same components—*i.e.*, Part A ($HfOCl_2$ or $ZrOCl_2$), Part B (H_2O_2), and Part C (H_2SO_4)—and once combined, the resulting coating materials will also necessarily contain the same components, including "metal ions with radiation sensitive ligands" as claimed. EX1002 ¶¶103-104. Accordingly, a

Pet., 37

> As explained by Dr. Holland, the HafSOx films of Stowers 2008 are the same as the HafSOx films of the '564 patent, i.e., they have the same components ($HfOCl_2$, H_2O_2, and H_2SO_4) and same metal to Hf to peroxide ratio. EX1002 ¶¶115-117.[16] Thus, they are the same films in all material respects. Accordingly, the HafSOx films

Pet., 44

> As explained by Dr. Holland, the ZircSOx and HafSOx films of Stowers 2008 are the same as the ZircSOx and HafSOx films of the '564 patent, *i.e.*, they have the same components ($HfOCl_2$ or $ZrOCl_2$, H_2O_2, and H_2SO_4) and same metal to peroxide ratio. EX1002 ¶123. Thus, they are the same films in all material respects.

Pet., 47

	Stowers 2008	'564 Patent
Metal Concentration	0.5 M EX1008, 68	0.16 M (Zr) 0.15 M (Hf) EX1001, 21:59, 64
Rests	15 minute rests after each addition. EX1008, 68	5 minute rests after each addition. EX1001, 21:23-55
Pre-exposure bake	None disclosed	40-200° C for 0.1-5 minutes 50° C EX1001, 22:20-21, 23:36-37.
Post-exposure bake	300° C for 5 minutes EX1008, 68-69	40-200° C for 1-5 minutes 75° C EX1001, 22:43, 23:38
Spin coating conditions	3000 rpm for 30 seconds, EX1008, 68	100 RPM for 5 seconds and then 3000 RPM for 30-60 seconds EX1001, 22:17-20
Substrate	silicon wafer chips or silicon coupons EX1008, 68	Five inch silicon wafers EX1001, 22:7
Metal to peroxide ratio	1 to 0.75 EX1008, 68	1 to 0.66-0.88 (Zr) 1 to 6.62-8.81 (Hf) EX1002, ¶38 (calculations based on EX1001, 21:10-67 (Example 1)); POPR, 29 n.4 (noting the error in the calculations); EX2011, 123:6-124:12 (Dr. Holland admitting the error).[9]

POR, 33-34

POR, 32-35; Sur-Reply, 10-13

Petitioner Did Not Prove That the Films Are Identical

Reply Disregards Differences

ratios, and (5) have different baking conditions. But none of these alleged differences change the resulting film's chemistry. EX1040, ¶¶41-51. Coatings made from precursor solutions having concentrations of either 0.5 M hafnium or 0.15 M hafnium both form HafSOx materials. EX1040, ¶42; EX1034, 2. The different rest times are inconsequential; they merely allow more "ligand exchange" time. EX1040, ¶¶46-48. As to coating speeds, the '564 patent discloses an additional 5-second, 100 RPM spin, which merely provides more time to "spread the resist across the wafer." EX1001, 22:17-20; EX1040, ¶49. And Inpria cherry-picks parts of Stowers 2008 while ignoring others to assert that there are differences in the baking conditions. EX1040, ¶50. Stowers 2008 discloses a prebake of 100 ºC and a post-exposure bake of 50 ºC[2], within the '564 patent's pre- and post-bake protocol (40 - 200 ºC). EX1008, 70; EX 1001, 22:20-43. Accordingly, the HafSOx and ZircSOx coating materials of Stowers 2008 and '564 patent are the same in all material respects and necessarily have the same properties. EX1002 ¶¶101-104, EX1040, ¶51.

Reply, 12

	Stowers 2008	'564 Patent
Metal Concentration	0.5 M EX1008, 68	0.16 M (Zr) 0.15 M (Hf) EX1001, 21:59, 64
Rests	15 minute rests after each addition. EX1008, 68	5 minute rests after each addition. EX1001, 21:23-55
Pre-exposure bake	None disclosed	40-200° C for 0.1-5 minutes 50° C EX1001, 22:20-21, 23:36-37.
Post-exposure bake	300° C for 5 minutes EX1008, 68-69	40-200° C for 1-5 minutes 75° C EX1001, 22:43, 23:38
Spin coating conditions	3000 rpm for 30 seconds, EX1008, 68	100 RPM for 5 seconds and then 3000 RPM for 30-60 seconds EX1001, 22:17-20
Substrate	silicon wafer chips or silicon coupons EX1008, 68	Five inch silicon wafers EX1001, 22:7
Metal to peroxide ratio	1 to 0.75 EX1008, 68	1 to 0.66-0.88 (Zr) 1 to 6.62-8.81 (Hf) EX1002, ¶38 (calculations based on EX1001, 21:10-67 (Example 1)); POPR, 29 n.4 (noting the error in the calculations); EX2011, 123:6-124:12 (Dr. Holland admitting the error).[9]

POR, 33-34

POR, 33-34; Sur-Reply, 11-13

Petitioner Did Not Prove That the Films Are Identical

Dr. Holland's Conclusory Disregard of Rest Times

46. Dr. Banerjee also opines that the differences in amount of rest time in the methods of forming precursor solutions (15 minutes in Stowers 2008 and 5 minutes in the '564 patent) could result in different coating films. EX2009, ¶35. I disagree. As I explained in my first declaration, both Stowers 2008 and the '564 patent disclose the same sequential addition of materials: (1) $HfOCl_2$ or $ZrOCl_2$ is mixed with H_2O_2 and allowed to rest, (2) H_2SO_4 was added to the solution and again allowed to rest, and (3) the solutions are diluted with ultrapure water. EX1002, ¶¶102-103. Stowers explains that the rest times "allow for ligand exchange" EX1008, 68. Accordingly, the 15 minutes rest period in Stowers 2008 merely allows more time for ligand exchange, and does not "result in different coating films" as Dr. Banerjee suggests.

EX1040, ¶46

Dr. Holland's New Reference

47. The importance in the sequential addition during forming the precursor solutions is made clear by Dr. Stowers' later publications. For example, Dr. Stowers later explained that a "HafSOx solution is formed by the **sequential addition** of aqueous $HfOCl_2$, H_2O_2, and H_2SO_4." EX1019, 1. As Dr. Stowers explains, the peroxide *prevents* hafnium tetramers from polymerizing and then the sulfate links the tetramers:

EX1040, ¶47

Dr. Holland Recognized Importance of Ligand Exchange

Q. And your understanding of the ligand exchange that you are referring to in that next sentence to be, for instance, peroxides going onto the hafnium or zirconium?

A. Correct. Connected to them.

Q. Is that ligand exchange important?

A. Yes.

Q. Why?

A. Because the ligand -- the peroxide ligands are known to be the photosensitive material that causes the reactivity in the resist.

Q. It's important for those ligands to be exchanged onto the hafnium ions, right?

A. Correct.

EX2017, 70:21-71:9

Petitioner Did Not Prove That the Films Are Identical

Dr. Holland's Conclusory Disregard of Initial Spin

49. I understand that Inpria has argued that the spin coating conditions could also affect the resulting films. POR, 33-34. Yet, the only difference between the spin coating conditions in Stowers 2008 and the '564 patent, is that the '564 patent includes an initial 100 RPM spin for five seconds. *Compare* EX1008, 68 *with* EX1001, 22:7. As the '564 patent explains, this "spreads the resist across the wafer." EX1001, 22:17-20. Accordingly, this will not change the composition of the resulting films.

EX1040, ¶49

Dr. Holland Recognized Importance of Initial Spin

Q. And in the next sentence, you say: "As the '564 patent explains, this spreads the resist across the wafer," right?

A. That is correct.

Q. Why would a POSA want to spread the resist across the wafer?

A. It would probably make a more uniform coating. So it's -- it's honestly something in that time frame where we used to just do one spin, and then we learned later on that doing just a light spin first to evenly put it on and then spin it gives us a better coating.

EX2017, 73:14-24

Petitioner Did Not Prove That the Films Are Identical

Dr. Stowers Email About Magic Sauce Supports Patent Owner

From: Andrew Grenville
To: Jason Stowers
Subject: Re: Futher HafSOx Reference
Date: Wednesday, February 24, 2010 3:49:09 AM
Importance: High

---

thanks for the heads up. At least that part is covered by the patent application. We just need to redouble our efforts on shoring up the IP. I do feel we are now in a much better position to tackle that.

Let's plan to talk at 9:45am tomorrow re the plan for Albany. Sorry to cut you off earlier. I'll look at your material beforehand. (the dropbox stuff is still downloading -- it's a slow connection).

Also, I had good discussions with Jacques tonight and he answered some of your questions re thickness, preparation, etc. (we can discuss). Among other things we also now have good pull from Samsung and from ASML/Zeiss senior management, which will help Roel get through any hoops. I met with Roel for an hour this morning, and he's clearly pretty motivated to get it on the ADT.

Andrew

On Feb 23, 2010, at 9:14 PM, Jason Stowers wrote:

FYI,
My Dissertation is now past its 1 year publication embargo.

You can find it :
https://urldefense.com/v3/__http://ir.library.oregonstate.edu/jspui/handle/1957/9543__;!!JB8VoVbPfh38FcDZRpZ1rQ!xhdHSKrmk5HFm2OeIwswEcg4kUDuz0OWtomoqzr1zq-ujw82A7lFUzm03VuN1gW_kiD4VVSxbnjC545kQLSoZJz6DQ$

Relevant magic sauce recipe is on page 68. Doug had me leave it vague.

Jason

EX2008, 6

Claim 1 – Radiation Sensitive Ligands

- Stowers 2008 Is Not Prior Art
- Claim 1 – Petitioner's "Same Films" Inherency Theory
- **Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient**
- Claim 1 – Exposure … Alters the Chemical Properties
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of no More Than 100 mJ/cm^2

Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient

Petition Is Conclusory

A POSA would also understand that the peroxide groups in Stowers 2008's precursor solution is a radiation sensitive ligand. EX1002 ¶100. 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, 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.*[11] Therefore, Stowers 2008 discloses a "coating material compris[ing] metal ions with radiation sensitive ligands."[12]

[11] An extinction coefficient "is a property that determines how strongly a material absorbs radiation at a particular wavelength." EX1002 ¶100.

Pet., 35

Dr. Holland Adds No Support

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."

EX1002, ¶100

POR, 37; Sur-Reply, 13-14

Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient

Dr. Holland Could Not Explain Theory

Q. So I guess my question is why is it necessarily the case that if you expect the extinction coefficient to change with the addition of peroxide, why that means, necessarily, peroxide is radiation sensitive as a ligand?

MR. BREGMAN: Objection.

A. I don't know. I just have what I've got written here, so explaining it -- especially since he says it's different -- expect it to be different -- doesn't say in which direction it's different.

EX2011, 148:8-17; *see also id.* 147:4-156:3

Dr. Banerjee Explains Theory Is Nonsensical

45. It does not logically, or scientifically, follow that if a mixture (e.g., HafSOx plus peroxide) is "expected" to have a different extinction coefficient than the original material (e.g., HafSOx), that the added material (peroxide) is a "radiation sensitive ligand." Different materials have different properties, including how strongly the material absorbs radiation. For instance, water, which absorbs radiation at a different strength than a metal, does not become a "radiation sensitive ligand" even if it is added to a metal and the extinction coefficient of water + metal is "expected" to be different than the extinction coefficient of the metal alone.

EX2009, ¶45

Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient

Reply Repeats Argument

Inpria alleges that Lam advances a "flawed 'extinction coefficient' theory." POR at 37. Not so. As Dr. Holland explained, and Dr. Banerjee agreed with, the "extinction coefficient is a property that determines how strongly a material absorbs radiation at a particular wavelength." EX1002, ¶100; EX1033, 161:3-7. This measurement indicates the material's sensitivity to radiation. EX1040, ¶53. Accordingly, because the extinction coefficient changes when peroxide is added, a POSA would understand the peroxide to be "radiation sensitive." *Id.*

Reply, 14

Dr. Holland Includes New Reference

53. First, I disagree that the change in extinction coefficient described by Stowers 2008 fails to indicate that the films are "radiation sensitive." Dr. Banerjee cites no authority for his opinion. Rather, the extinction coefficient is an indication of the sensitivity of the material to radiation:

> Photoresists contain photoactive components, which absorb light of a specific wavelength and upon absorption undergo chemical transformation. As a result of such transformations, the extinction coefficient of the active ingredient changes. In addition, photoresists typically contain other components which may or may not absorb light, but do not undergo chemical reactions as result of exposure and whose extinction coefficients are therefore constant.

EX1035, 679. Accordingly, where the photoresists do not undergo chemical reactions (i.e. are not "radiation sensitive), one would expect the extinction coefficients to be constant. In Stowers 2008, however, the extinction coefficients change upon the addition of peroxide, indicating that peroxide is radiation sensitive.

EX1040, ¶53

Sur-Reply, 14

Claim 1 – Radiation Sensitive Ligands – Extinction Coefficient

New Reply Arguments Should Be Rejected

Inpria's own expert admits that the peroxide group in Stowers 2008's working solutions is a radiation sensitive ligand. EX1033, 165:21-166:11 ("We now know that [peroxide] is radiation sensitive."). Although Dr. Banerjee implies that Dr. Stowers was unaware that peroxide was radiation sensitive, recognition of an inherent property is not required. *EMI Grp. N. Am., Inc. v. Cypress Semiconductor Corp.*, 268 F.3d 1342, 1349–51 (Fed. Cir. 2001). Even so, Stowers 2008 describes peroxide as radiation sensitive. EX1008, 46; EX1040, ¶54. And it explains that the photosensitive HafSOx and ZircSOx materials were adapted by "changing the chemistries to a peroxide based system." EX1008, 143. Thus, a POSA would understand that the peroxide in Stowers 2008's working solutions is a radiation sensitive ligand. EX1040, ¶54.

Reply, 13

Moreover, Dr. Stowers' later publications confirm the Stowers 2008 coatings' peroxide are radiation sensitive. EX1040, ¶56. In 2009, Dr. Stowers explained that, for HafSOx and ZircSOx, "the mechanism that leads to negative tone patterning is dependent on the presence of peroxide" because "beam-induced decomposition and elimination of peroxide promotes condensation reactions, cross-linking of metal-oxo bridges, and the production of three-dimensional framework structures." EX1010, 21. And in 2018 Dr. Stowers explained HafSOx includes a "radiation sensitive peroxide ligand." EX1019, 2. Accordingly, based on Dr. Stowers' own characterizations, the peroxide ligand in the coatings of 2008 was "radiation sensitive."

Reply, 14

Sur-Reply, 14

Petitioner's Alternative Rationales Also Fail

- Stowers 2008 Is Not Prior Art
- Claim 1 – Petitioner's "Same Films" Inherency Theory
- Claim 1 – Radiation Sensitive Ligands
- **Claim 1 – Exposure … Alters the Chemical Properties**
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of no More Than 100 mJ/cm^2

Claim 1 – Exposure … Alters the Chemical Properties

Petitioner Wrongly Assumes Patterning Necessarily Means Alters the Chemical Properties

Second, Stowers 2008 discloses patterning of ZircSOx films by exposure to **UV radiation**. EX1008, 68 ("Patterning by **UV light** was achieved…"). Stowers 2008 "found that ZircSOx could be patterned by **UV light** in either **positive or negative tone**." *Id.*, 70. Stowers 2008 further 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., 70-72. In other words, Stowers 2008 discloses that exposure of a ZircSOx 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. EX1002 ¶108.

Pet., 40-41

Dr. Banerjee Testifies Patterning Can Be Chemical or Physical Change

41. For example, a person of ordinary skill in the art would have known that such exposure to UV or EUV radiation could alter a physical property of the material as opposed to a chemical property. (EX2006, 1:18-20 ("The chemical ***or physical*** properties of the photoresist can be changed by being exposed to light.") (emphasis added).)

EX2009, ¶41

Claim 7 – High Absorption of EUV Radiation

- Stowers 2008 Is Not Prior Art
- Claim 1 – Petitioner's "Same Films" Inherency Theory
- Claim 1 – Radiation Sensitive Ligands
- Claim 1 – Exposure … Alters the Chemical Properties
- **Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists**
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Claim 7 – High Absorption of EUV Radiation

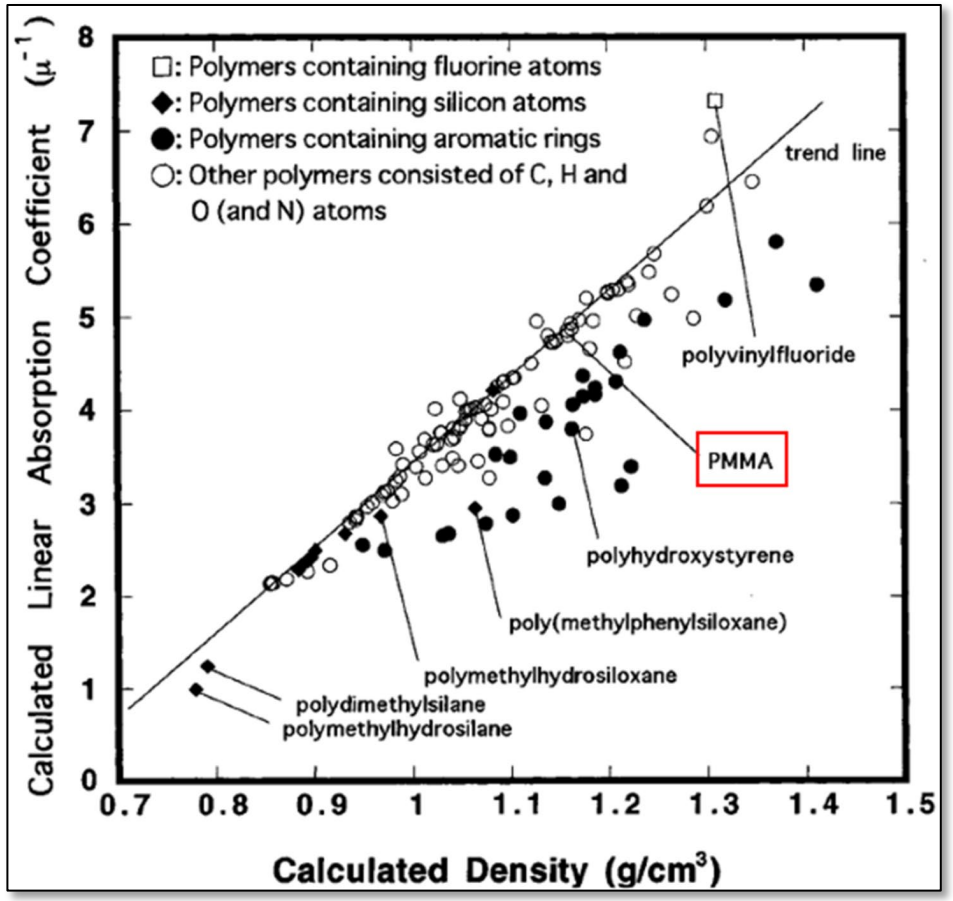
Density Inherency Theory

Stowers 2008 discloses that "ZircSOx and particularly HafSOx have a **higher density** than other resists like…**PMMA (1.19 g/cm^3)**" and recites their "**assumed**" densities of "**4 g/cm^2 for ZircSOx** and **5 g/cm^3 for HafSOx**." EX1008, 90; 83 ("PMMA [is] a traditional polymer electron beam resist."). A POSA would have known that as **density increases, EUV absorbance increases**. Indeed, the trend is generally linear as shown below:

Pet., 52

EUV). Based on this linear trend, a POSA would have known that ZircSOx and HafSOx films have a higher absorption of EUV relative to PMMA (polymethyl methacrylate, which is a conventional organic resist) because ZircSOx and HafSOx films have a higher assumed mass density than PMMA. EX1008, 90; EX1002 ¶¶136-137.

Pet., 53



Pet., 53

Claim 7 – High Absorption of EUV Radiation

Dr. Holland Admits EUV Absorption Can Vary

So there are certain elements that might be in these things that would cause them to have different responses.

Q. Okay. So it's not necessarily the density alone that governs the EUV absorption; right?

MR. BREGMAN: Objection. Form.

A. It is one of the most common -- if you look at that, the majority of them fall on the line, and only if they have certain elements in them that have different absorption of the EUV is it affected.

EX2011, 182:13-22

A. The general trend is the higher the density, the higher the absorption, and that does change depending on other atoms, as I mentioned earlier. There are specific atoms that are very absorptive.

EX2011, 225:21-24

Dr. Banerjee Shows Not Inherent

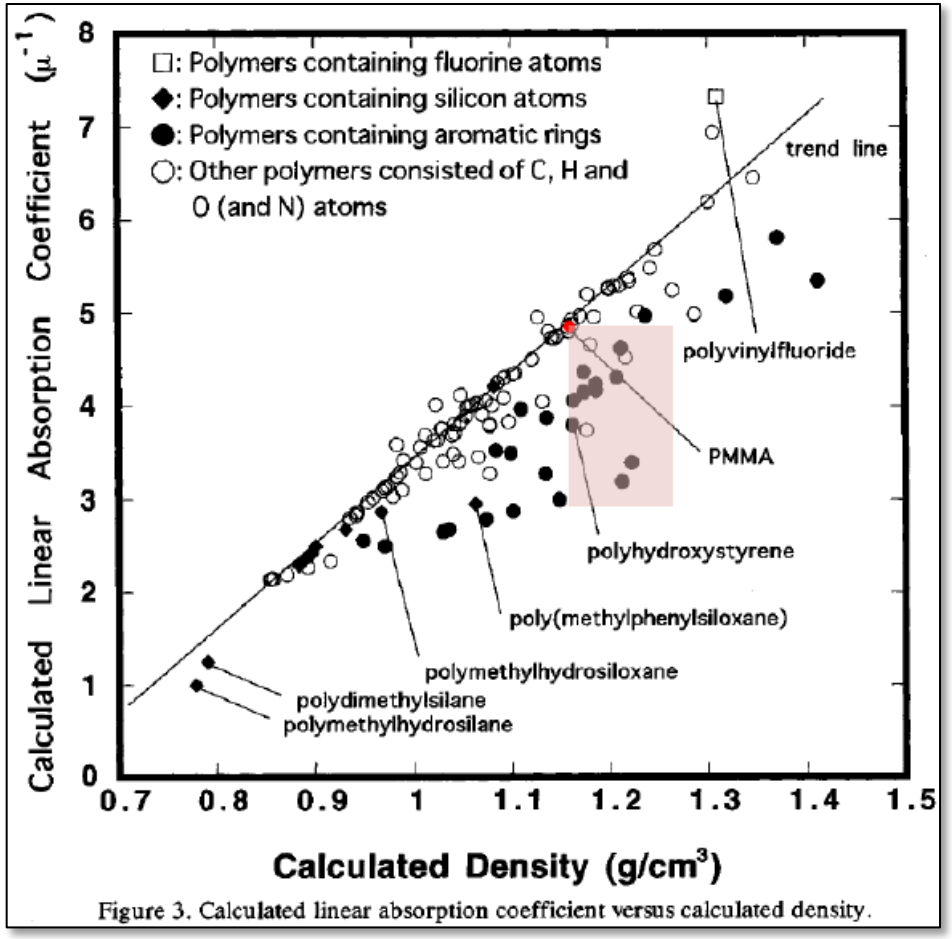


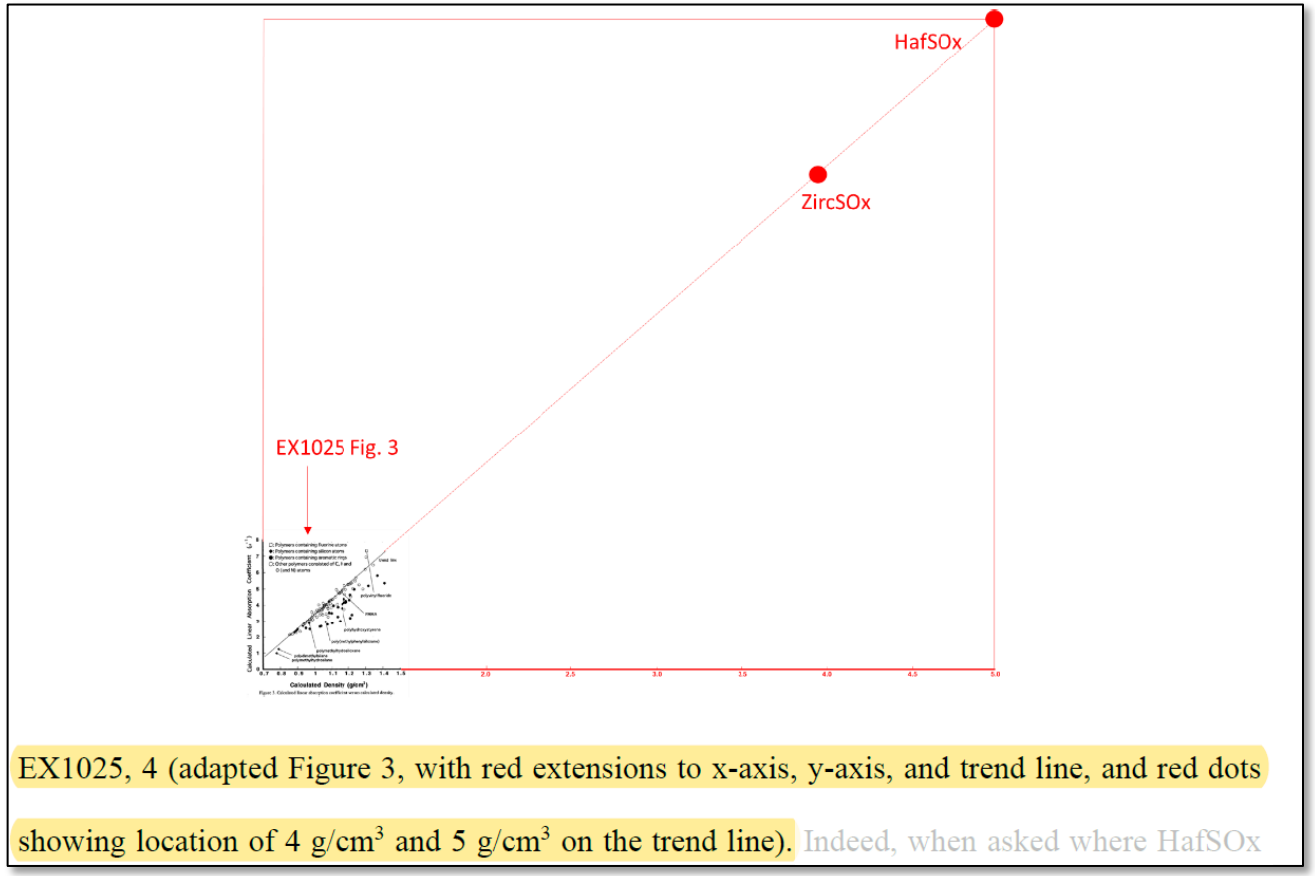
Figure 3. Calculated linear absorption coefficient versus calculated density.

EX2009, ¶50

POR, 42-44; Sur-Reply, 14-15

Claim 7 – High Absorption of EUV Radiation

Dr. Holland's Unsupported Extrapolation in Reply



EX1025, 4 (adapted Figure 3, with red extensions to x-axis, y-axis, and trend line, and red dots showing location of 4 g/cm^3 and 5 g/cm^3 on the trend line). Indeed, when asked where HafSOx

EX1040, ¶77

4	Q. Once you get to higher density and off that
5	chart, for example, were you showing -- for ZircSOx and
6	HafSOx here, how do you know the trend is linear in the
7	upward direction at those higher densities?
8	A. We just drew it that way. Partly also because,
9	you know, Dr. Banerjee pointed to a location off the
10	chart in that general direction in XY also. So we were
11	agreeing with him on that.
12	Q. But you don't know whether the trend is linear
13	at those much higher densities, do you?
14	A. I haven't calculated them. I haven't done -- I
15	have not done experiments on these to get that answer,
16	so I would have to do experiments to understand them.

EX2017, 100:4-16

Claim 7 – High Absorption of EUV Radiation

Petitioner's Reply

correlation between density and EUV absorption is a "trend." Yet, when asked where HafSOx and ZircSOx would fall on the graph, Dr. Banerjee pointed to a location well off the chart (Pet. at 53; EX1025, Fig. 3), admitting that the Stowers 2008 materials have high absorption relative to conventional radiation-based resists. EX1033, 179:8-180:6. Although there may be some variation in the "trend" where

Reply, 16

Dr. Banerjee Did Not Admit Inherency

Q Could you draw on figure 3 in Exhibit 1025 where HafSOx would fall?

MR. WOLFE: Objection. Scope.

A It would be somewhere over here maybe (indicating).

Q So off, off the page?

A Off the page, yes.

Q On both the x and y-axis is what you showed; correct?

A Right, but one should not conflate the absorption properties of an inorganic material like HafSOx with these materials which are all organic.

EX1033, 180:8-20

Q Do you know what the calculated linear absorption coefficient of HafSOx and ZircSOx are?

A No, not offhand.

Q So you don't know whether it is higher or lower than the dots on this graph then; is that correct?

MS. PATITUCCI: Objection. Leading.

A That's correct.

EX1033, 188:4-11

Sur-Reply, 15

Claim 7 – High Absorption of EUV Radiation

Petitioner Failed to Prove 2011 Films Are the Same

> Indeed, this is similar to what named inventor Stowers described in a 2011 publication. EX1022, 3 (noting a calculated mass density of 4.7 g/cm^3 for HafSOx and stating that "[t]his mass density and the compositional information are used to **calculate EUV absorption**…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 more absorptive**."); EX1002 ¶138.

Pet., 53-54

> For 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. 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/cm^3. This mass density and the compositional information are used to calculate EUV absorption from the Center for X-Ray Optics database,[11] 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 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.

EX1022, 3

POR, 44; Sur-Reply, 16

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2

- Stowers 2008 Is Not Prior Art
- Claim 1 – Petitioner's "Same Films" Inherency Theory
- Claim 1 – Radiation Sensitive Ligands
- Claim 1 – Exposure … Alters the Chemical Properties
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- **Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2**

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Petition Relies Only on ZircSOx Dose

> Stowers 2008 reports that patterning of the ZircSOx "materials with electron beam lithography **produced excellent results**." EX1008, 127. "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 µC/cm²**." *Id.*, 89.

> Given that Stowers 2008 discloses effective patterning of ZircSOx with an e-beam dose corresponding to an **EUV equivalent dose of less than 25 mJ/cm²**, a POSA would reasonably expect that those same ZircSOx films "can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm²." EX1002 ¶146. The '103 provisional admits as much:

Pet., 54-55

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Petition Applies HafSOx Correlation

> As Stowers himself confirmed in 2011, an "e-beam [or electron beam] **dose of 249 µC/cm²** (30 keV)…has been **well characterized to correspond to an EUV dose of 25 mJ/cm²**." EX1022, 7. Thus, if an e-beam dose of 249 µC/cm² "corresponds" to an EUV dose of 25 mJ/cm², a POSA would in turn understand that an **e-beam dose of 112 µC/cm² "corresponds" to an EUV dose that is less than 25 mJ/cm²**, *i.e.*, "no more than 100 mJ/cm²." EX1002 ¶145.

Pet., 55

> For 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. We have directly measured the electron density of these materials

EX1022, 3

9	Q. Would you agree that this article is about
10	hafnium?
11	A. This article is referring to hafnium as the
12	photoresist metal.

EX2011, 203:9-12

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Petitioner's New Reply Theories Should Be Rejected

> Stowers 2008 reports that ZircSOx can be patterned with an e-beam dose of 112 μC/cm². EX1008, 89. Similarly, HafSOx was patterned with e-beam doses of 60 μC/cm² and 300 μC/cm². *Id.* at 99-100. Dr. Stowers' 2011 article relates to both HafSOx and ZircSOx, using the generic term "MSOx." EX1022, 3. Thus, the correlation between an e-beam dose of 249 μC/cm² and EUV dose of 25 mJ/cm² applies to *both* HafSOx and ZircSOx. EX1040, ¶83.

Reply, 18

> However, even if the e-beam to EUV dose applies only to HafSOx, Dr. Stowers also explained that the dose **improves** with zirconium-based formulations. EX1014, 3 ("For HafSOx, $E_{1:1}$=90 mJ/cm²;…and for ZircSOx, $E_{1:1}$=25 mJ/cm².").

Reply, 18

Sur-Reply, 17-18

Petitioner Has Not Established Any Ground of Invalidity

Ground 1	Petitioner Fails to Show Anticipation by the ’888 Publication for Claims 1-12
Ground 2	Petitioner Fails to Show Anticipation Over Stowers 2008 for Claims 1-5, 7-10, and 12
Ground 3	Petitioner Fails to Show Obviousness Over Stowers 2008 for Claims 1-10 and 12
Ground 4	Petitioner Fails to Show Obviousness Over Stowers 2008 and Stowers 2009 for Claim 8
Ground 5A/B	Petitioner Fails to Show Anticipation or Obviousness Over Trikeriotis for Claims 1, 3, 6-7, 9, and 11-12
Motion to Amend	Petitioner’s 112, 102, and 103 Arguments Fail

Pet., 3; Inst. Dec., 5

Ground 5A/B – Petitioner's Trikeriotis Arguments Are Deficient

- Trikeriotis (EX1024) Is Not Prior Art
- Petitioner's Ground(s) Are Facially Deficient
- Claim 1 – Radiation Sensitive Ligands
- Claim 6 – Average Thickness of 5 nm to 25 nm
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Trikeriotis (EX1024) Is Not Prior Art

- **Trikeriotis (EX1024) Is Not Prior Art**
- Petitioner's Ground(s) Are Facially Deficient
- Claim 1 – Radiation Sensitive Ligands
- Claim 6 – Average Thickness of 5 nm to 25 nm
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Trikeriotis (EX1024) Is Not Prior Art

Petition Relies on Exhibit 1024

4. Trikeriotis (EX1024)

Trikeriotis published on March 25, 2010. EX1006 ¶¶59-67; *see also* EX1031, Cover. Trikeriotis is therefore prior art to the '564 patent under pre-AIA § 102(a) (if the '564 patent is entitled to its purported August 5, 2010 or June 1, 2010 priority date) or post-AIA § 102(a)(1) (if the '564 patent is not entitled to its priority date).

Pet., 23

I. Ground 5: Claims 1, 3, 6-7, 9, 11-12 Are Anticipated and/or Rendered Obvious by Trikeriotis

As shown below, Trikeriotis anticipates and/or renders obvious claims 1, 3, 6-7, 9 and 11-12.

Pet., 58

b) "coating material comprises metal ions with radiation sensitive ligands"

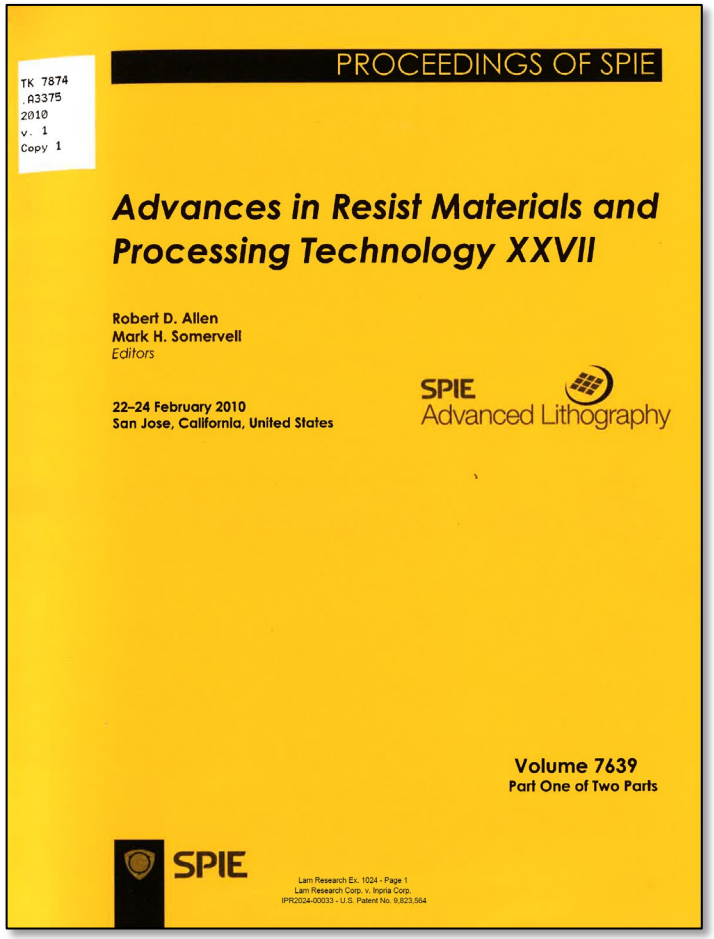
Trikeriotis discloses "an inorganic resist made of **hafnium oxide nanoparticles** that can be used both for optical (DUV or EUV) and electron beam lithography." EX1024, 16. Trikeriotis states that "**[h]afnium oxide nanoparticles** are used as a core to build the inorganic nanocomposite into an imageable photoresist" and that "a variety of **organic ligands** can be used to control the surface chemistry of the final product." EX1024, 15. "**The absorption coefficient of the films depends on the ligand**…" *Id.*, 18 (*i.e.*, the ligands are radiation sensitive).

Pet., 58

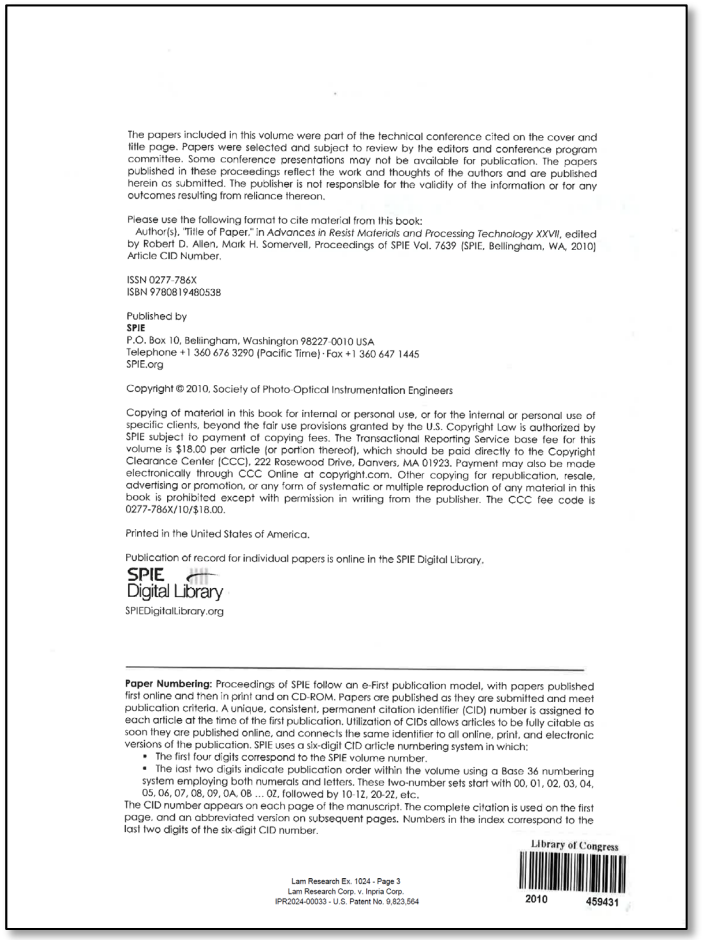
POR, 28-31; Sur-Reply, 18-19

Trikeriotis (EX1024) Is Not Prior Art

Exhibit 1024 Is a Print Copy From the Library of Congress



EX1024, 1



EX1024, 3

Trikeriotis (EX1024) Is Not Prior Art

Dr. Hall-Ellis Testified That Exhibit 1024 Was Available After Priority Date

VII. DOCUMENT 3: EXHIBIT 1024 ("TRIKERIOTIS")

59. Attached hereto is a true and correct copy of the conference paper titled "Development of an Inorganic Photoresist for DUV, EUV, and Electron Beam Imaging" by Markos Trikeriotis, Woo Jin Bae, Evan Schwartz, Marie

The exhibit filed in this proceeding as Exhibit 1024 is a true and correct copy of the conference paper. I obtained this copy of the article from the Library of Congress. Specifically, the text of the conference paper is complete; no pages are

EX1006, ¶59

62. Attachment 3A shows that the two-part *Proceedings of SPIE -- the International Society for Optical Engineering*, volume 7639 was cataloged at the Library of Congress on September 9, 2010, and the cataloging process was completed on September 21, 2010, as shown in field 955. Therefore, this volume was publicly available to users at the Library of Congress on that date.

EX1006, ¶62

Congress on September 9, 2010. In view of Attachment 3B, the two-part volume 7639 of the *Proceedings of SPIE -- the International Society for Optical Engineering* was publicly available on or shortly after September 21, 2010, because by that date it had been received, cataloged, and indexed at the Library of Congress and made part of the OCLC bibliographic database.

EX1006, ¶63

Trikeriotis (EX1024) Is Not Prior Art

Lam Abandons Hall-Ellis in Reply – Relies on Print Cover and Patrick Franzen

A. Trikeriotis is Prior Art

Inpria wrongly argues that Trikeriotis is not prior art. Trikeriotis on its face confirms that it was published *before* the June 10, 2010 Priority Date:



EX1024, 1 (dated 22-24 February, 2010). Further, a declaration from SPIE's

Reply, 19

9. Exhibit A to this declaration is a true and correct copy, from the SPIE Digital Library and SPIE's business records, of a paper authored by M. Trikeriotis, et al., "Development of an inorganic photoresist for DUV, EUV, and electron beam imaging," first published on the SPIE Digital Library in SPIE Proceedings Vol. 7639 titled "Advances in Resist Materials and Processing Technology XXVII," on 25 March 2010. The paper was later published in the print version of Vol. 7639 which published on 3 May 2010.

EX1043, ¶9

18	A So "published" there means the physical
19	copies arrived at our warehouse, in which case we
20	would then be able to distribute them to potential
21	customers.

12	Q Do you know how much time would have
13	passed between when you received these copies from
14	the printer and then when you distributed them?
15	A I do not.

EX2018, 30:18-31:15

Sur-Reply, 18-19

Trikeriotis (EX1024) Is Not Prior Art

Reply & MTA Sur-Reply Shift Reliance to Electronic Publication

EX1024, 1 (dated 22-24 February, 2010). Further, a declaration from SPIE's Director of Publications and Platforms confirms that Trikeriotis was presented as part of a conference on 22-24 February 2010, and was later published online on 25 March 2010 and published in print on 3 May 2010. EX1043, ¶¶1, 8-9. Accordingly,

Reply, 19

PO's challenge to the availability of Trikeriotis also conflates two identical versions—the print and electronic version. Reply at 7. While the print version "was received at the SPIE from the printer on May 3, 2010" and "was publicly available on or shortly after September 21, 2010," it is undisputed that ***the identical electronic version was publicly available by March 25, 2010***. EX1006, ¶¶59-66.

MTA Sur-Reply, 8

9. Exhibit A to this declaration is a true and correct copy, from the SPIE Digital Library and SPIE's business records, of a paper authored by M. Trikeriotis, et al., "Development of an inorganic photoresist for DUV, EUV, and electron beam imaging," first published on the SPIE Digital Library in SPIE Proceedings Vol. 7639 titled "Advances in Resist Materials and Processing Technology XXVII," on 25 March 2010. The paper was later published in the print version of Vol. 7639 which published on 3 May 2010.

EX1043, ¶9

60. The Trikeriotis paper is available and can be downloaded from the International Society for Optical Engineering (SPIE) website[21] and the digital repositories *ResearchGate*[22] and *Semantic Scholar*.[23] The SPIE website indicates a March 25, 2010, publication date.

[21] https://www.spiedigitallibrary.org/conference-proceedings-of-spie/7639/76390E/Development-of-an-inorganic-photoresist-for-DUV-EUV-and-electron/10.1117/12.846672.short?SSO=1

EX1006, ¶60

Sur-Reply, 18-19

Trikeriotis Ground(s) Are Facially Deficient

- Trikeriotis (EX1024) Is Not Prior Art
- **Trikeriotis Ground(s) Are Facially Deficient**
- Claim 1 – Radiation Sensitive Ligands
- Claim 6 – Average Thickness of 5 nm to 25 nm
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … at a Dose of No More Than 100 mJ/cm^2

Trikeriotis Ground(s) Are Facially Deficient

Petitioner's Missing Obviousness Ground

> In Ground 5, Lam alleges that "Trikeriotis anticipates *and/or renders obvious* claims 1, 3, 6-7, 9, and 11-12," Pet., 58 (emphasis added), telegraphing the weakness of its anticipation position. Lam, however, completely fails to provide any analysis as to why the claims are obvious in view of Trikeriotis. Novelty under 35 U.S.C.

POR, 47

- **"[I]t does not follow that every technically anticipated invention would also have been obvious."**

  Cohesive Techs., Inc. v. Waters Corp., 543 F.3d 1351, 1363 (Fed. Cir. 2008)

- **"[T]he initial petition [must] identify 'with particularity' the 'evidence that supports the grounds for the challenge to each claim."**

  Intelligent Bio-Sys., Inc. v. Illumina Cambridge Ltd., 821 F.3d 1359, 1369 (Fed. Cir. 2016)

> particularity either anticipation or obviousness, Lam's Reply section discussing Trikeriotis, Reply, 20-27, is nearly double the length of the same section in its Petition, Pet., 58-62. This underscores that Lam is improperly attempting to plug

Sur-Reply, 19

Claim 1 – Radiation Sensitive Ligands

- Trikeriotis (EX1024) Is Not Prior Art
- Trikeriotis Ground(s) Are Facially Deficient
- **Claim 1 – Radiation Sensitive Ligands**
- Claim 6 – Average Thickness of 5 nm to 25 nm
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2

Claim 1 – Radiation Sensitive Ligands

Petition Only Quotes Without Analysis

b) "coating material comprises metal ions with radiation sensitive ligands"

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, 16. Trikeriotis states that "**[h]afnium oxide nanoparticles** are used as a core to build the inorganic nanocomposite into an imageable photoresist" and that "a variety of **organic ligands** can be used to control the surface chemistry of the final product." EX1024, 15. "**The absorption coefficient of the films depends on the ligand**…" *Id.*, 18 (*i.e.*, the ligands are radiation sensitive). Therefore, Trikeriotis discloses a "coating material compris[ing] metal ions with radiation sensitive ligands." EX1002 ¶152.

Pet., 58-59

Dr. Holland Adds No Support or Analysis

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.

EX1002, ¶152

POR, 50-51

Claim 1 – Radiation Sensitive Ligands

Dr. Holland Could Not Explain Further – Points to DPAP

Q. And then, what are the radiation-sensitive ligands in Trikeriotis?
A. I don't remember what he used. Sorry. I haven't found yet what he uses that is photosensitive.
Okay. It says here, "nanoparticle films with DPAP" -- I'm not going read the whole word out -- as a photo-inhibitor [sic] act both as a positive and negative tone photoresists."

EX2011, 215:13-20

Q. Okay. So that photoactive material being DPAP would be the radiation-sensitive ligands per the claims?
MR. BREGMAN: Objection. Mischaracterizes testimony.
A. That's the best I can do on here because he doesn't state it differently.

EX2011, 218:18-23

Trikeriotis

The nanoparticle films with 2,2-dimethoxy-2-phenyl acetophenone (DPAP) as a photoinitiator act both as positive and negative tone photoresists. Films with the desired thickness are prepared and then baked at 130°C for 60 sec on a hot plate. After exposure under DUV light (254 or 193 nm), development in isopropyl alcohol or t-amyl alcohol gives a negative tone image. For 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, 20

Ober

displacement is associated with a solubility change. Similarly, if a photoradical generator is used that produces benzoate as a product (e.g., 2,2-dimethoxy-2-phenylacetophenone), this can also displace the methacrylate ligand. There is a strong cor-

EX1027, 2

Claim 1 – Radiation Sensitive Ligands

Ober Contradicts Petitioner's Theory

SPIE Newsroom

10.1117/2.1201409.005552

New oxide nanoparticle extreme-UV photoresists achieve high sensitivity

Christopher Ober and Emmanuel Giannelis

High-performance photoresists made from metal oxide nanoparticles offer high-sensitivity lithography at extreme-UV wavelengths by using a new ligand-based patterning mechanism.

There remains strong debate regarding which patterning technology will be used in next-generation electronics. The International Technology Roadmap for Semiconductors (ITRS) predicts that feature dimensions of less than 20nm will be required for semiconductor processing within the next two years. Three possible approaches are featured in the ITRS report: nanoimprint patterning, in which a resist film is molded on top of a substrate using micromachined masters; directed self-assembly, which exploits the self-assembly properties intrinsic to block copolymers; and extreme-UV (EUV) patterning—the most traditional strategy of the three methods under development—which depends on short-wavelength radiation (13nm) to create a solubility change in exposed areas.

EUV patterning enables the formation of small-scale patterns with the arbitrary shapes enabled by light-based lithography. Recent improvements to light sources (in terms of both reliability and power) as well as new photoresists, such as those based on chemically amplified materials and nanoparticles, are driving significant interest in this technology. At present, the challenge lies in creating a photoresist that works well under EUV radiation, is highly sensitive, and improves on the line-edge roughness and line-width roughness (LER/LWR) performance of most EUV resists. Because of the way that materials interact with short-wavelength EUV radiation, it is believed that the incorporation of higher mass elements would be beneficial to EUV photoresists. These elements provide improvements to optical properties and increase the energy harvesting abilities of the photoresists, enabling more of the applied energy to photochemically induce solubility changes and thereby increase sensitivity.

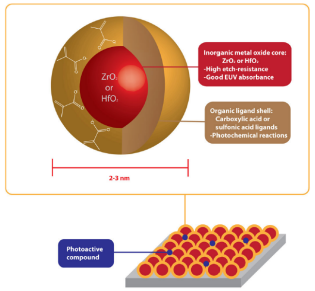


Figure 1. Schematic of the extreme-UV (EUV) nanoparticle photoresist with its core metal oxide and the organic ligand surrounding the core. ZrO_2: Zirconium dioxide. HfO_2: Hafnium oxide.

Strong interest has recently developed in the use of metal oxide nanoparticles as photoresists. These materials enable the incorporation of higher mass elements. Initial studies have demonstrated that hafnium and zirconium oxide nanoparticles can be patterned to very high resolution—in some cases down to 10nm—with excellent image fidelity and LER.[1] Researchers are working to improve the sensitivity of the current water-based system, which depends on peroxides for its patterning process. We 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

Continued on next page

Lam Research Ex. 1027 - Page 1
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

EX1027, 1

Petitioner Asserts Ober Shows Films of Trikeriotis

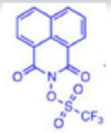
as it shows a sensitivity $D_{0.8}$ **of less than 25 mJ/cm²**. EX1002 ¶161. Moreover, as confirmed by Ober and Giannelis, "[w] have found that a hafnium oxide (HfO_2) core with a diameter of 2nm, surrounded by organic ligands (binding molecules), **can be patterned at EUV wavelengths with extremely high sensitivity (<5mJ/cm²)**." EX1027, 1-2 (referring to the films of Trikeriotis).

Pet., 62

[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 (<5mJ/cm²)." EX1027 at 1-2 (referring to the films of the Trikeriotis reference).

EX1002, ¶161 n.6

Claim 1 – Radiation Sensitive Ligands

Photoactive Compound () Is Radiation Sensitive, Not the "Organic Ligands" ()

Dr. Banerjee

59. Here, Ober shows the nanoparticles in orange, the organic ligands in red, and the photoactive compounds in blue interspersed in the film between the nanoparticles. This schematic makes clear that it is the "photoactive compounds" as a result of the radiation exposure by "ligand-displacement." Critically, this figure shows nothing happening to the red organic ligands themselves based on exposure, other than they are displaced by the blue photoactive compound that was broken down by radiation exposure. For these reasons, Ober shows that the "organic ligands" Dr. Holland points to in Trikeriotis are actually not the "radiation sensitive" material of Trikeriotis.

EX2009, ¶59

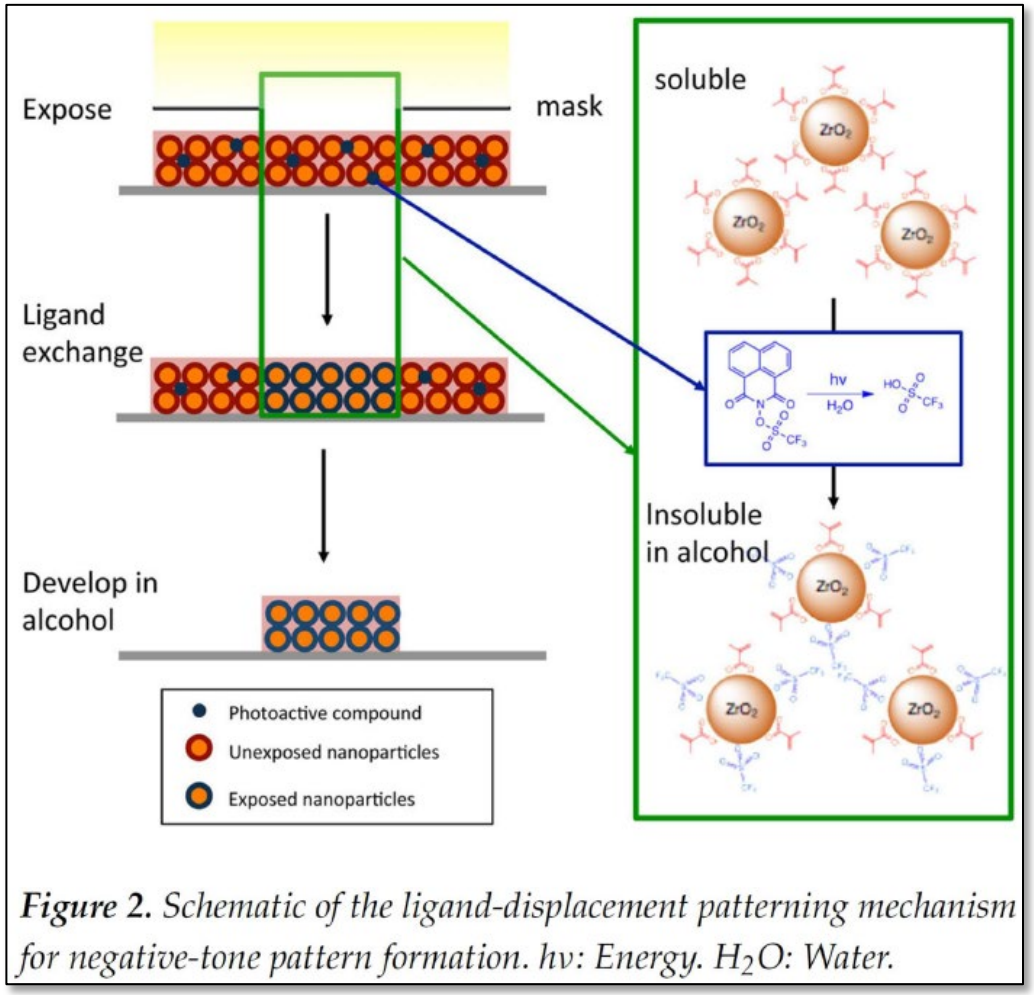


Figure 2. *Schematic of the ligand-displacement patterning mechanism for negative-tone pattern formation. hv: Energy. H_2O: Water.*

Ex. 1027, 2 (Fig. 2)

Claim 1 – Radiation Sensitive Ligands

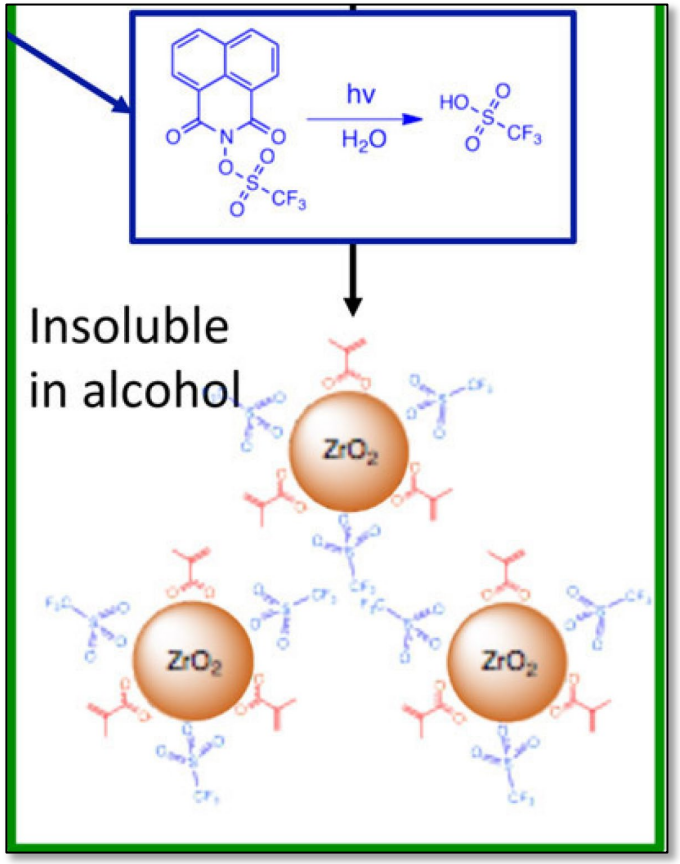
Petitioner Did Not Prove Blue Ligands () Are Photosensitive

Reply

However, both the red "starting ligands" and blue "new ligands" **are ligands**, where the radiation cleaves part of the blue ligand. *Id.*; EX1040, ¶61. Dr. Banerjee admits that the "new ligands" are ligands which are modified by radiation. EX1033, 181:19-182:7, 183:15-20. Accordingly, even under Inpria's theory, Trikeriotis's ligands are "radiation sensitive."

Reply, 24

Ober



EX1027, Fig. 2

Dr. Banerjee

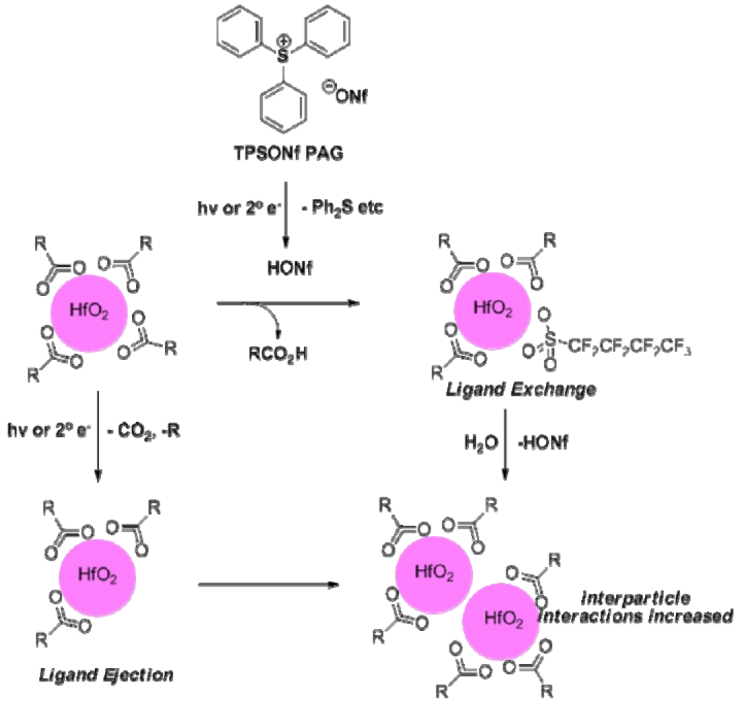
Q What is ligand displacement?
A That's shown on this cartoon view on the right-hand green rectangle. So the inorganic shells are surrounded with the ligand shown in, I guess I'll call it pink. That's not what where the photochemistry is happening; it's happening in the blue, molecule in the blue box in the middle, and then the byproducts of that photochemical reaction in blue are displacing some of these attached pink ligands attached to the inorganic core, and that's the lower half of that figure.
Q So the blue ligands replace the pink ligands; is that right?
A The blue photoactive compound byproducts displace the pink ligand.

EX1033, 181:19-182:11

Sur-Reply, 21-22

Claim 1 – Radiation Sensitive Ligands

Board Should Reject New Decarboxylation Theory in Reply



As shown above, radiation causes decarboxylation of the ligands. EX1036, 6; EX1040, ¶62. Accordingly, the organic ligands of the Trikeriotis nanoparticle are necessarily "radiation sensitive." *Id.*

Reply, 25

Sur-Reply, 19-20

Claim 6 – Average Thickness of 5 nm to 25 nm

- Trikeriotis (EX1024) Is Not Prior Art
- Trikeriotis Ground(s) Are Facially Deficient
- Claim 1 – Radiation Sensitive Ligands
- **Claim 6 – Average Thickness of 5 nm to 25 nm**
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2

Claim 6 – Average Thickness of 5 nm to 25 nm

Petition Conclusory

3. Claim 6

Claim 6 depends on claim 1 and requires that "the average thickness is from **5 nm to 25 nm**." As noted above, in Figure 8, **"the film that was used was only 30 nm thick**." EX1024, 21. It would have been within the routine skillset of a POSA to experiment with the spin rate and time to obtain the desired thickness. EX1002 ¶157.

Pet., 60

Dr. Holland Adds No Analysis

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.")

EX1002, ¶157

Trikeriotis

film. The film that was used was only 30 nm thick to minimize the absorbance and reflection of light. Currently, optimization of the photoresist formulation is underway to pattern 60 nm features on thicker films.

EX1024, 21

POR, 56-57

Claim 6 – Average Thickness of 5 nm to 25 nm

New Reply Theory

2. Average Thickness of 5 nm to 25 nm (claim 6)

Inpria cherry picks statements from Trikeriotis that a POSA would have been motivated to create "thicker films," not thinner films. POR at 56. Although Trikeriotis was testing a variety of thicknesses, including those thicker than 30 nm, Trikeriotis explained that "[t]he trend of ever decreasing feature sizes in subsequent lithography generations is paralleled by the **need to reduce resist thickness** to prevent pattern collapse." EX1024, 15. Accordingly, film thickness is a result-effective variable that a POSA would have found obvious to optimize. *In re Applied Materials, Inc.*, 692 F.3d 1289, 1297 (Fed. Cir. 2012) ("A recognition in the prior art that a property is affected by the variable is sufficient to find the variable result-effective."). Specifically, a POSA would have been motivated to prevent pattern collapse by optimizing the photoresist to reduce its thickness.[3] EX1002, ¶157. Therefore, it would have been obvious to reduce the thickness to 5 nm to 25 nm.

[3] The Petition further describes the motivation to reduce film thickness in detail. Petition at 49-51.

Reply, 21

ABSTRACT

The trend of ever decreasing feature sizes in subsequent lithography generations is paralleled by the need to reduce resist thickness to prevent pattern collapse. Thinner films limit the ability to transfer the pattern to the substrate during etch steps, obviating the need for a hardmask layer and thus increasing processing costs. For the 22 nm node, the critical aspect ratio will be less than 2:1, meaning 40-45 nm thick resists will be commonplace. To address this problem, we

EX1024, 15

G. Ground 3: Claims 1-10, 12 Are Obvious Over Stowers 2008

1. Independent Claim 1

Pet., 48;

Pet., 48-51 (full section regarding Stowers 2008 claim 1)

Claim 7 – High Absorption of EUV Radiation

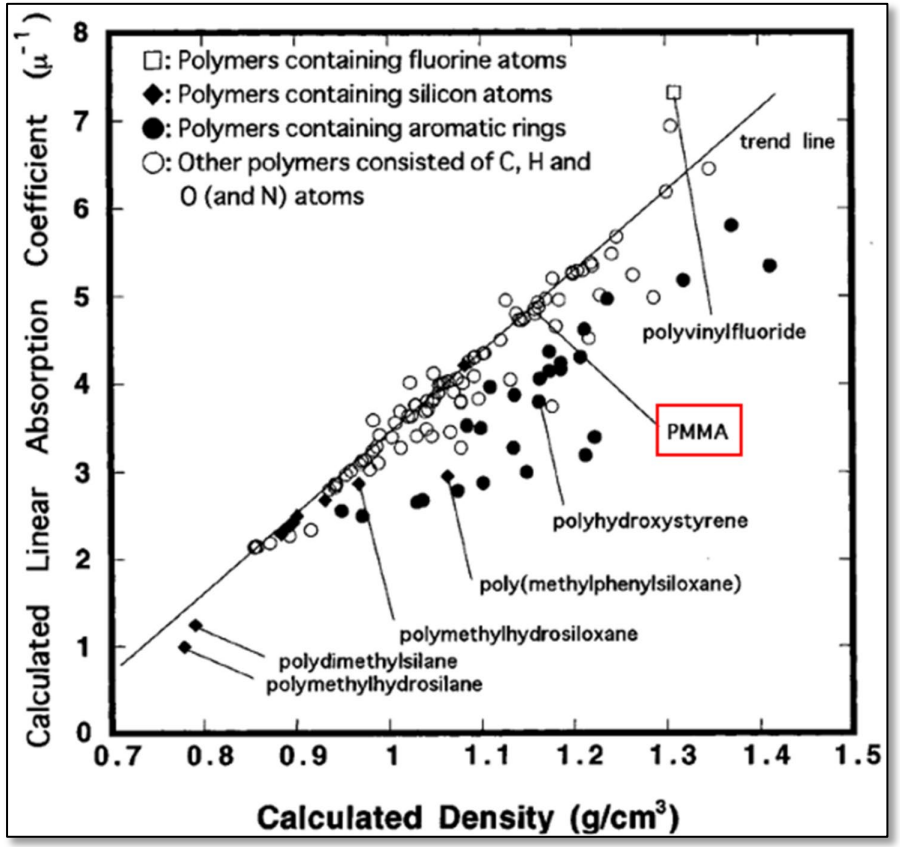
- Trikeriotis (EX1024) Is Not Prior Art
- Trikeriotis Ground(s) Are Facially Deficient
- Claim 1 – Radiation Sensitive Ligands
- Claim 6 – Average Thickness of 5 nm to 25 nm
- **Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists**
- Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2

Claim 7 – High Absorption of EUV Radiation

Deficient Density Inherency Theory

Trikeriotis's films are based on hafnium oxide. A POSA would know hafnium oxide has a mass density of ~9.68 g/cm^3. *See, e.g.*, EX1026, 4. As explained above in Ground 3, POSA would have also known that PMMA, a conventional organic resist, has a mass density of ~ 1.19 g/cm^3. EX1008, 90. Since a POSA would have known that as the mass density increases, the EUV absorption increases (EX1025, Figure 3), a POSA would have known that hafnium oxide has a higher absorption of EUV than organic resists. EX1002 ¶158.

Pet., 60-61



EX1002, ¶136

Claim 7 – High Absorption of EUV Radiation

New Reply Theories Should Be Rejected

2. High Absorption of EUV Radiation

Inpria recycles the same arguments used in opposition to Stowers 2008—i.e., density does not correlate to EUV absorption. Inpria is mistaken. *See supra* at § IV.C.3. Additionally, because "[a]bsorption of EUV light in matter depends entirely on the atomic composition and the absorption cross section of elements," the Trikeriotis nanoparticles—which contain hafnium and have a significantly higher EUV absorbance than carbon—necessarily have higher EUV absorption than traditional organic resists. EX1044, 2; EX1040, ¶79.

Reply, 25-26

Q. I understand. So in paragraph 79, in those two figures, those are comparing elements, right?

A. That's correct.

Q. And it could have other things in the photoresists that affect the EUV absorption, right?

A. It could be.

EX2017, 106

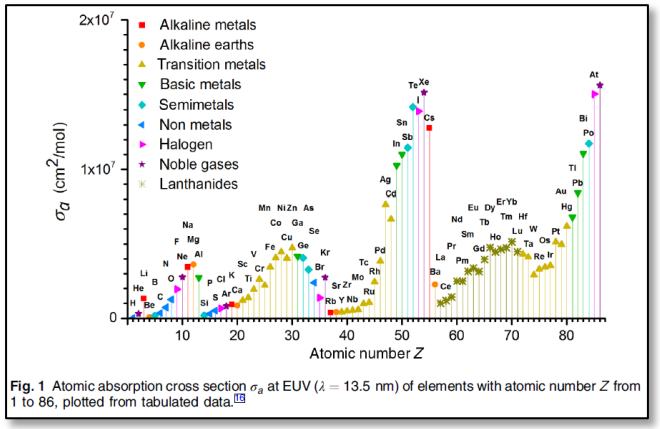
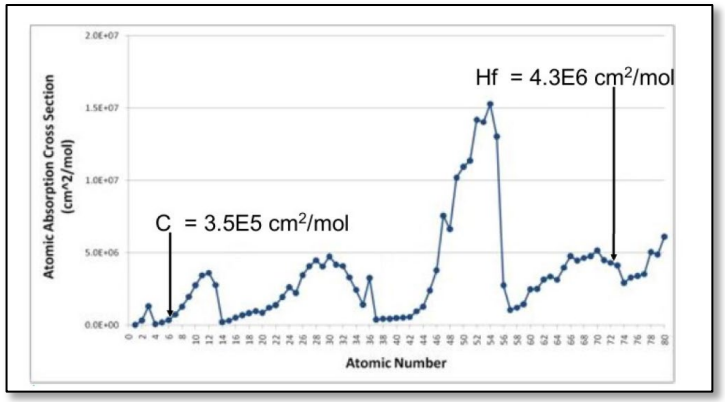


Fig. 1 Atomic absorption cross section σ_a at EUV (λ = 13.5 nm) of elements with atomic number Z from 1 to 86, plotted from tabulated data.[19]

EX1044, 2



EX1040, ¶79

Sur-Reply, 22-23

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2

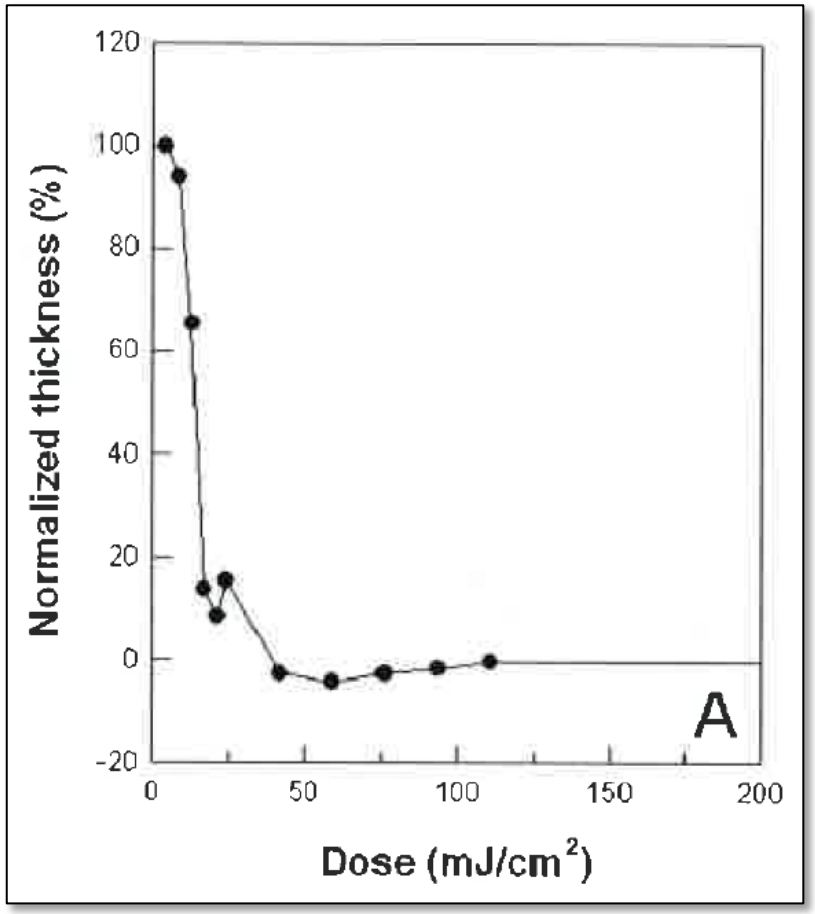
- Trikeriotis (EX1024) Is Not Prior Art
- Trikeriotis Ground(s) Are Facially Deficient
- Claim 1 – Radiation Sensitive Ligands
- Claim 6 – Average Thickness of 5 nm to 25 nm
- Claim 7 – High Absorption of EUV Radiation Relative to Conventional Radiation Based Resists
- **Claim 12 – Effectively Patterned … No More Than 100 mJ/cm^2**

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Petition Relied on "Sensitivity $D_{0.8}$" and Fig. 5A of Trikeriotis

than 100 mJ/cm².” Figure 5A of Trikeriotis shows that the discloses films could be patterned in positive tone with a 254 nm UV radiation dose of less than 100 mJ/cm² as it shows a sensitivity **$D_{0.8}$ of less than 25 mJ/cm²**. EX1002 ¶161. Moreover, as

Pet., 61-62

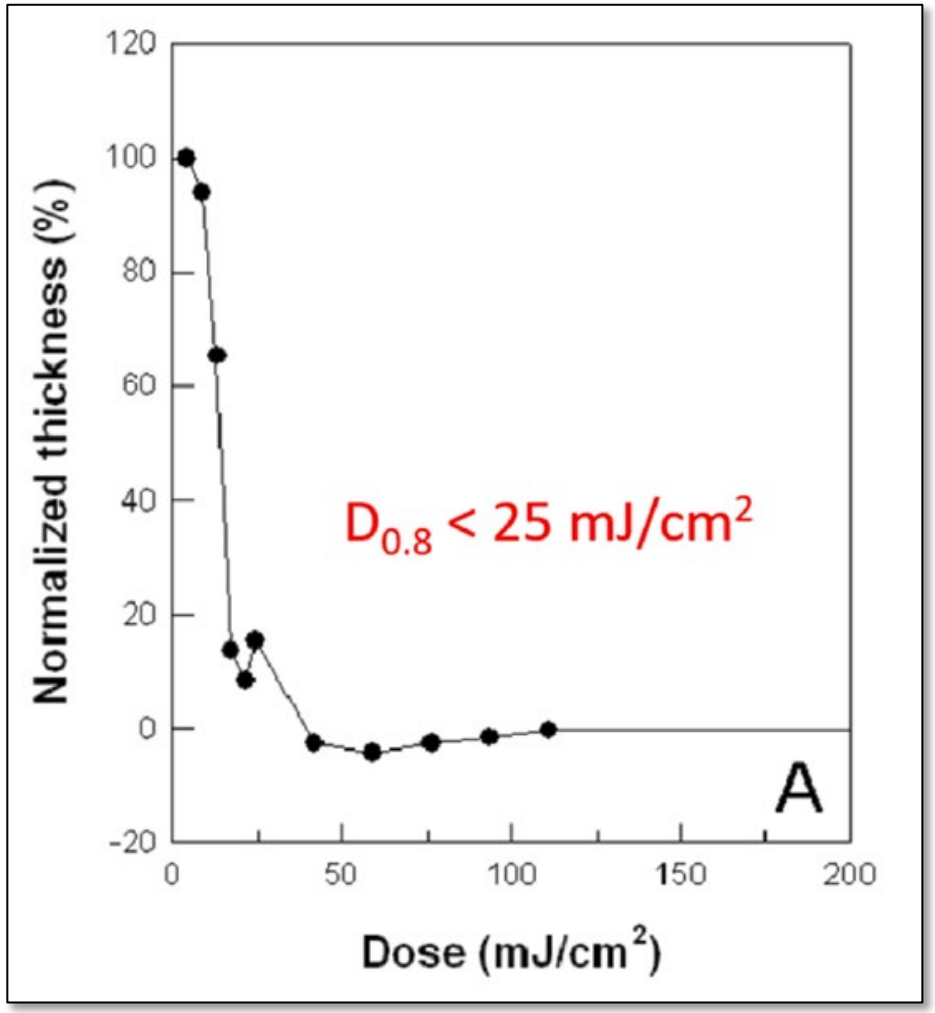


EX1024, Fig. 5A

POR, 57-58

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Dr. Holland Added $D_{0.8}$ Annotation But Could Not Explain



EX1002, ¶161.

18	Q. Sitting here today, do we have any way to know
19	what you meant by D 0.8 in paragraph 161 that was added
20	to the figure?
21	A. I'm going to have to go back and look. I'm
22	sorry. I do not remember. I'm sure at the time...
23	Q. But right now, you don't remember?
24	A. Correct; I don't remember right now.

9	Q. And did you -- and did you add that annotation
10	there in red?
11	MR. WOLFE: Objection. Leading.
12	A. So I added the D 08, and after reading back in
13	here, my guess is that that was supposed to be a D --
14	oh, what was the word there I wanted to use? Anyway,
15	the 08's a typo. I believe it's a 09.

EX2011, 228:18-24, 239:9-15

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Reply Presents New and Unsupported Explanation of $D_{0.8}$

> and Keszler referring to a $D_{0.8}$ of 290 μC/cm²). $D_{0.8}$ refers to the dose required for 80% exposed film to be soluble (for a positive tone resist) or insoluble (negative tone resist). EX1040, ¶86; EX1037, 43; EX1046, 1; EX1047, 186. Accordingly, Dr.

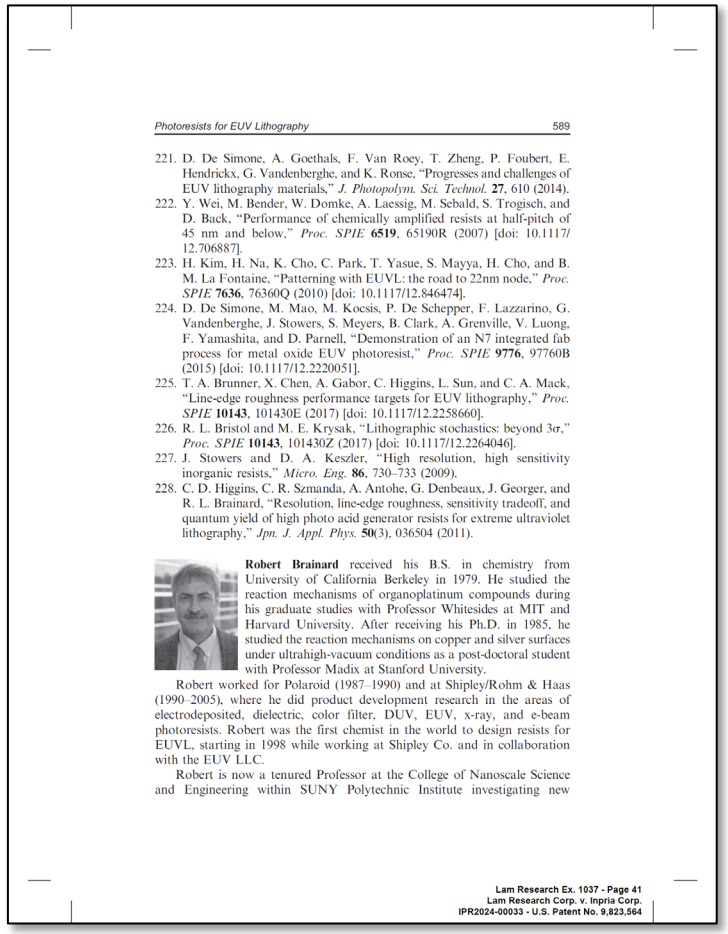
Reply, 27

> exposed regions have been removed by the developer (*i.e.*, a normalized thickness close to 0%). I added the notation of $D_{0.8} < 25$ mJ/cm² to show the dose required for 80% of the exposed film to be soluble (for a positive tone resist) or insoluble (for a negative tone resist). *See, e.g.*, EX1037, 43; EX1046, 1; EX1047, 186. In Trikeriotis Figure 5A, at a dose of less than 25 mJ/cm², the

EX1040, ¶86

Claim 12 – Effectively Patterned … No More Than 100 mJ/cm²

Lam's New Explanation of $D_{0.8}$ Is Unsupported



Photoresists for EUV Lithography 589

221. D. De Simone, A. Goethals, F. Van Roey, T. Zheng, P. Foubert, E. Hendrickx, G. Vandenberghe, and K. Ronse, "Progresses and challenges of EUV lithography materials," *J. Photopolym. Sci. Technol.* **27**, 610 (2014).
222. Y. Wei, M. Bender, W. Domke, A. Laessig, M. Sebald, S. Trogisch, and D. Back, "Performance of chemically amplified resists at half-pitch of 45 nm and below," *Proc. SPIE* **6519**, 65190R (2007) [doi: 10.1117/12.706887].
223. H. Kim, H. Na, K. Cho, C. Park, T. Yasue, S. Mayya, H. Cho, and B. M. La Fontaine, "Patterning with EUVL: the road to 22nm node," *Proc. SPIE* **7636**, 76360Q (2010) [doi: 10.1117/12.846474].
224. D. De Simone, M. Mao, M. Kocsis, P. De Schepper, F. Lazzarino, G. Vandenberghe, J. Stowers, S. Meyers, B. Clark, A. Grenville, V. Luong, F. Yamashita, and D. Parnell, "Demonstration of an N7 integrated fab process for metal oxide EUV photoresist," *Proc. SPIE* **9776**, 97760B (2015) [doi: 10.1117/12.2220051].
225. T. A. Brunner, X. Chen, A. Gabor, C. Higgins, L. Sun, and C. A. Mack, "Line-edge roughness performance targets for EUV lithography," *Proc. SPIE* **10143**, 101430E (2017) [doi: 10.1117/12.2258660].
226. R. L. Bristol and M. E. Krysak, "Lithographic stochastics: beyond 3σ," *Proc. SPIE* **10143**, 101430Z (2017) [doi: 10.1117/12.2264046].
227. J. Stowers and D. A. Keszler, "High resolution, high sensitivity inorganic resists," *Micro. Eng.* **86**, 730–733 (2009).
228. C. D. Higgins, C. R. Szmanda, A. Antohe, G. Denbeaux, J. Georger, and R. L. Brainard, "Resolution, line-edge roughness, sensitivity tradeoff, and quantum yield of high photo acid generator resists for extreme ultraviolet lithography," *Jpn. J. Appl. Phys.* **50**(3), 036504 (2011).

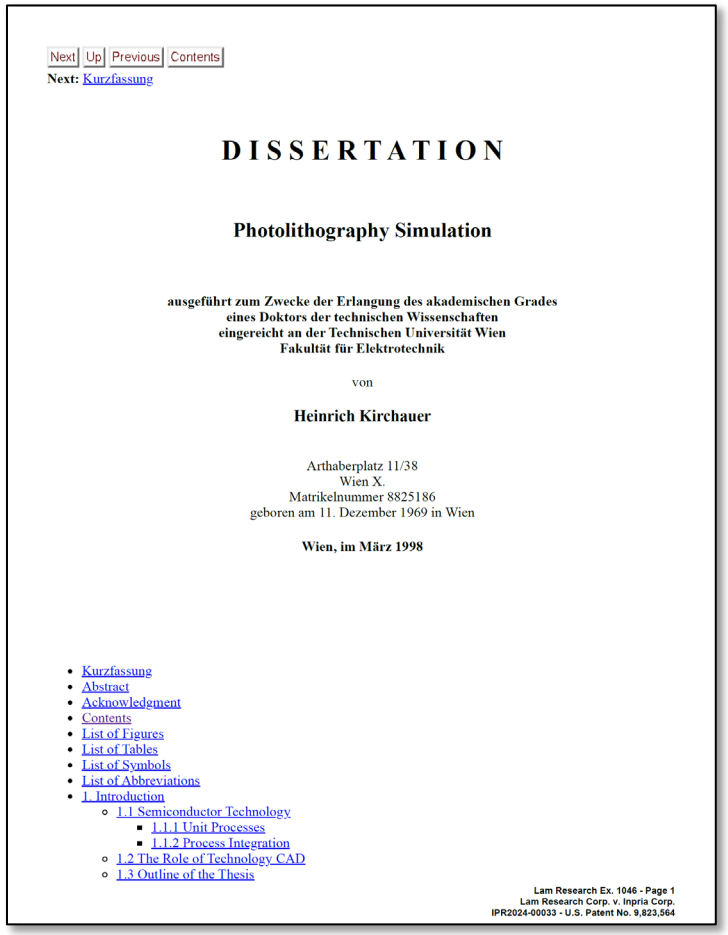
Robert Brainard received his B.S. in chemistry from University of California Berkeley in 1979. He studied the reaction mechanisms of organoplatinum compounds during his graduate studies with Professor Whitesides at MIT and Harvard University. After receiving his Ph.D. in 1985, he studied the reaction mechanisms on copper and silver surfaces under ultrahigh-vacuum conditions as a post-doctoral student with Professor Madix at Stanford University.

Robert worked for Polaroid (1987–1990) and at Shipley/Rohm & Haas (1990–2005), where he did product development research in the areas of electrodeposited, dielectric, color filter, DUV, EUV, x-ray, and e-beam photoresists. Robert was the first chemist in the world to design resists for EUVL, starting in 1998 while working at Shipley Co. and in collaboration with the EUV LLC.

Robert is now a tenured Professor at the College of Nanoscale Science and Engineering within SUNY Polytechnic Institute investigating new

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IPR2024-00033 - U.S. Patent No. 9,823,564

EX1037, 41 (final page of exhibit)



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Next: Kurzfassung

DISSERTATION

Photolithography Simulation

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der technischen Wissenschaften eingereicht an der Technischen Universität Wien Fakultät für Elektrotechnik

von

Heinrich Kirchauer

Arthaberplatz 11/38
Wien X.
Matrikelnummer 8825186
geboren am 11. Dezember 1969 in Wien

Wien, im März 1998

- Kurzfassung
- Abstract
- Acknowledgment
- Contents
- List of Figures
- List of Tables
- List of Symbols
- List of Abbreviations
- 1. Introduction
  - 1.1 Semiconductor Technology
    - 1.1.1 Unit Processes
    - 1.1.2 Process Integration
  - 1.2 The Role of Technology CAD
  - 1.3 Outline of the Thesis

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IPR2024-00033 - U.S. Patent No. 9,823,564

EX1046, 1 (Cover)



3.3.2
Photocuring

Photocuring refers to the methods employed for various practical applications that are based on the light-induced polymerization of low-molar-mass liquid compounds (monomers and oligomers), and result in the formation of rigid intermolecularly crosslinked materials that are insoluble in most solvents. The most important applications here include surface coatings, the preparation of printing plates, the curing of dental preventive and restorative systems, and microfabrication with the aid of stereolithography. Further detailed information on this topic is available in books and reviews [46,211–229]

In contrast to thermal curing, photocuring can be performed at ambient temperatures with solvent-free formulations. In many cases, photocuring processes that proceed within a fraction of a second have replaced the conventional thermal curing of solvent-containing formulations. The main industrially applied photocuring processes are based on four chemical systems that are converted into three-dimensional networks upon irradiation [225]: (i) unsaturated maleic/fumaric acid-containing polyesters (*UPEs*) dissolved in styrene; (ii) acrylate/methacrylate systems; (iii) thiol/ene systems; and (iv) epoxide- or vinyl ether-containing systems. In the first three systems, free-radical polymerizations are operative, whilst in the fourth system cationic species are involved (see Section 3.2.2.1). Industrially applied polymerizable formulations are composed of mixtures of monofunctional and multifunctional monomers and oligomers (Table 3.23) containing a photoinitiator and, if required, also additives such as polymers (pre-polymers, resins) and pigments. The composition of a formulation applied for microfabrication, as a typical example, is presented in Table 3.24. With regards to the thiol/ene systems, the mechanism of free radical thiol/alkene polymerization outlined in Scheme 3.44 is assumed to be operative [229]. Moreover, by employing polyfunctional thiol compounds it is possible to form very tough, abrasion-resistant coatings [217].

The UV-curing of coatings is widely used, and all types of substrate – including paper, plastic, and metal – are coated using this technique (Table 3.25). The main benefits of the method are that it delivers short production times, provides high-quality products, has low energy needs and equipment costs, and is also environment-friendly because of the greatly reduced emissions of volatile organic compounds (*VOCs*).

Silicones have the advantage of softness, biological inertness, good substrate wettability, and superb permeability of gases. Consequently, UV-cured silicones are suitable for various interesting product applications [229], including ophthalmic devices (hard and soft contact lenses, intraocular lens implants), gaskets, sealings, and optical fiber coatings. Photocurable formulations appropriate for the fabrication of such products contain siloxane derivatives bearing unsaturated carbon–carbon double bonds (Chart 3.13).

Apart from acrylate-based systems, which are cured by a free-radical mechanism, epoxide-based systems that are cured cationically are also used. Epoxide-based formulations yield excellent overprint varnishes on tin-free steel and aluminum for rigid packaging, especially when producing steel food cans and aluminum beer and

EX1047, 186 (Photocuring)

The Motion to Amend

Ground 1	Petitioner Fails to Show Anticipation by the ’888 Publication for Claims 1-12
Ground 2	Petitioner Fails to Show Anticipation Over Stowers 2008 for Claims 1-5, 7-10, and 12
Ground 3	Petitioner Fails to Show Obviousness Over Stowers 2008 for Claims 1-10 and 12
Ground 4	Petitioner Fails to Show Obviousness Over Stowers 2008 and Stowers 2009 for Claim 8
Ground 5A/B	Petitioner Fails to Show Anticipation or Obviousness Over Trikeriotis for Claims 1, 3, 6-7, 9, and 11-12
Motion to Amend	Petitioner’s 112, 102, and 103 Arguments Fail

The Motion to Amend

- Proposed Amendments
- Motion to Amend Is Compliant
- Petitioner's Section 112 Arguments Fail
- Petitioner's Section 102 and 103 Arguments Fail
  - Petitioner's Stowers 2008 Arguments Fail
  - Petitioner's Trikeriotis Arguments Fail
  - Petitioner's Keszler Arguments Fail

Proposed Amendments

- **Proposed Amendments**
- Motion to Amend Is Compliant
- Petitioner's Section 112 Arguments Fail
- Petitioner's Section 102 and 103 Arguments Fail
  - Petitioner's Stowers 2008 Arguments Fail
  - Petitioner's Trikeriotis Arguments Fail
  - Petitioner's Keszler Arguments Fail

Proposed Amendments

Proposed Amended Claim 13 (substitute for Claim 1)

13. 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 of about 25 nm~~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.

Proposed Amended Claim 19 (substitute for Claim 8)

19. The structure of claim 13~~1~~ having a molar concentration ratio of radiation sensitive ligands to metal ion~~ to radio-sensitive ligand ratio~~ of at least about 2.

MTA, 13-14

The Motion to Amend Is Compliant

- Proposed Amendments
- **Motion to Amend Is Compliant**
- Petitioner's Section 112 Arguments Fail
- Petitioner's Section 102 and 103 Arguments Fail
  - Petitioner's Stowers 2008 Arguments Fail
  - Petitioner's Trikeriotis Arguments Fail
  - Petitioner's Keszler Arguments Fail

The Motion to Amend Is Compliant

Proposed Amended Claim 19 (substitute for Claim 8)

19. The structure of claim 13~~1~~ having a molar concentration ratio of radiation sensitive ligands to metal ion ~~to radio-sensitive ligand ratio~~ of at least about 2.

MTA, 14

II. SCOPE OF DEPENDENT CLAIM ENLARGED - NOT BROADENING

As pointed out above, a claim will be considered a broadened reissue claim when it is greater in scope than **each and every** claim of the patent to be reissued. A corollary of this is that a claim which has been *broadened in a reissue as compared to its scope in the patent* is not a broadened reissue claim if it is narrower than, or equal in scope to, any other claim which appears in the patent. A common example of this is where dependent claim 2 is broadened via the reissue (other than the addition of a process step to convert an intermediate to a final product), but independent claim 1 on which it is based is not broadened. Because a dependent claim is construed to contain all the limitations of the claim upon which it depends, claim 2 must be at least as narrow as claim 1 and is thus not a broadened reissue claim.

MPEP § 1412.03 (II)

"In the similar contexts of claim reissuance and reexamination, which likewise disallow a patent owner from enlarging the scope of its claims, we have explained that a claim 'is broader in scope than the original claim[ ] if it contains within its scope any conceivable apparatus or process which would not have infringed the original patent.'"

Sisvel Int'l S.A. v. Sierra Wireless, Inc., 81 F.4th 1231, 1237 (Fed. Cir. 2023) (citations omitted).

MTA, 8, 14; MTA Reply, 12

Petitioner's Section 112 Arguments Fail

- Proposed Amendments
- Motion to Amend Is Compliant
- **Petitioner's Section 112 Arguments Fail**
- Petitioner's Section 102 and 103 Arguments Fail
  - Petitioner's Stowers 2008 Arguments Fail
  - Petitioner's Trikeriotis Arguments Fail
  - Petitioner's Keszler Arguments Fail

Petitioner's Section 112 Arguments Fail

- **Petitioner's Section 112 Arguments Fail**
  - **Radiation Sensitive Ligands**
  - **Metal Ions with Radiation Sensitive Ligands**
  - **Enablement**
  - **About 25**
  - **Metal Ions**
  - **Terms of Degree**
    - **High Absorption**
    - **Conventional Resists**
    - **Effectively Patterned**
  - **IPXL Method/Apparatus**

Petitioner's 112 Arguments Fail – Radiation Sensitive Ligands

Petitioner Fails to Support Its Argument That the Claims Are Directed to a Broad Genus

> Claim 13 uses functional language to claim a broad genus of compounds based on the desired result—*i.e.*, "ligands" that have the function of being "radiation sensitive." Mot. at 6. Proposed substitute claims 14-15 and 17-23 do not include any

Opp., 3

> Petitioner's expert Dr. Holland testified to the meaning of ligand and the breadth of the genus of ligands. EX1040, ¶146. Her testimony that the field is "unpredictable" and that "[t]here are practically an infinite number of potential ligands" in the genus stands unrebutted and is a basic fact that any POSA would know. EX1040, ¶144-6.

MTA Sur-Reply, 2

> 146. A POSA would understand that, as used in the '564 patent, a "ligand" is an atom or molecule with a functional group that binds to a central atom—typically a metal—in a coordination complex. Given this understanding, a POSA would know that there are nearly an infinite number of atoms or molecules that could qualify as a ligand.

EX1040, ¶146

MTA Reply, 1-2

Petitioner's 112 Arguments Fail – Radiation Sensitive Ligands

Petitioner Has Not Shown Specification Guidance Is Inadequate

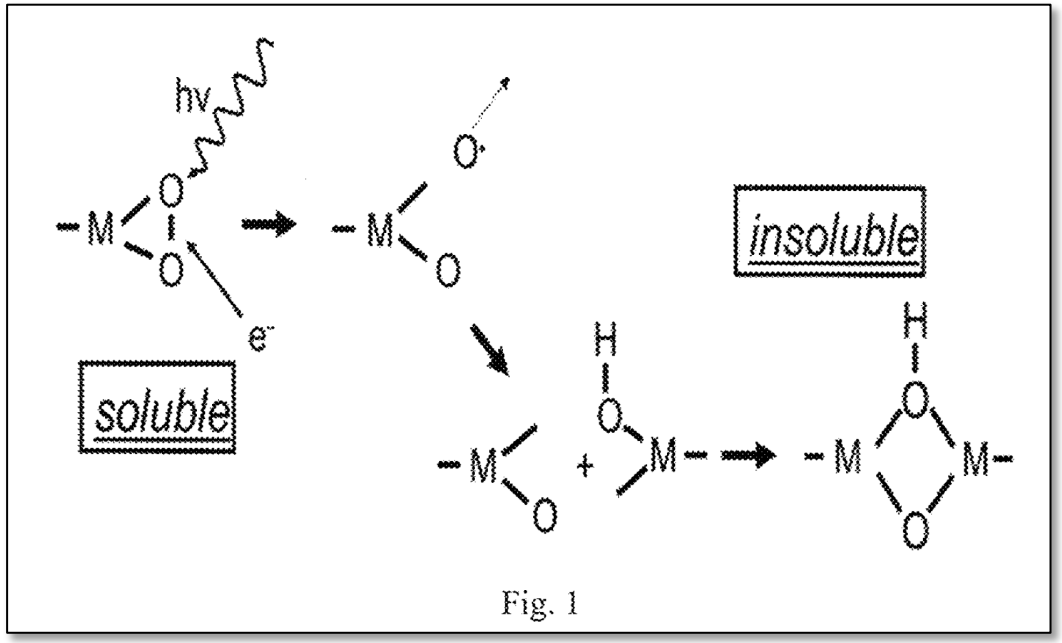


Fig. 1

FIG. **1** is a schematic drawing depicting a metal cation bonded to a ligand, where M represents a metal atom and O represents an oxygen atom, undergoing a condensation reaction triggered by energy absorption from radiation.

EX1001, Fig. 1, 3:6-9

retaining convenient processing to form coatings. Radiation sensitive ligands of particular interest have a peroxide group, —O—O—. As noted above in the context of FIG. **1**, energy from absorbed radiation can break the oxygen-oxygen bond. As the peroxide groups are broken, the cor-

EX1001, 12:11-15

The chemically simplest ligand composition would be hydrogen peroxide, H_2O_2, which is soluble in water. Additional peroxide-based ligands include, for example, organic compositions and/or inorganic compositions. In some embodiments, inorganic peroxide-based ligands can be desirable since carbon can be disadvantageous for many devices. If an inorganic peroxide is used as a radiation sensitive ligand, the risk of carbon contamination from the radiation sensitive ligand is avoided. Suitable inorganic peroxide ligands include, for example, peroxysulfate (SO_5H^-), peroxydisulfate ($S_2O_8^{-2}$), peroxychlorates (ClO_5H^-), or the like or combinations thereof. The precursor

EX1001, 12:22-33

Petitioner's 112 Arguments Fail – Metal Ions With Radiation Sensitive Ligands

Petitioner Provides No Support for Theory of Ligand Radiation Sensitivity Dependent on Metal

> ¶149. That is, while a ligand may be radiation sensitive on its own or in combination with certain metal ions, it may lack radiation sensitivity when combined with other metal ions. EX1040 ¶149. Second, the claims require that a "coating material"—

Opp., 5

> 149. As discussed above, due to the unpredictability of chemistry and chemical properties, combining certain elements or functional groups into a molecule can affect the properties of the molecule in unpredictable ways. As relevant here, combining different metal ions with different ligands could affect the radiation sensitivity of the ligands. As an example, A POSA would understand that a ligand that has radiation sensitivity as an independent molecule, or when used with one type of metal ion, may not have the same radiation sensitivity when used with a different metal ion.

EX1040, ¶149

Petitioner's 112 Arguments Fail – Metal Ions With Radiation Sensitive Ligands

Dr. Holland's Conclusory Testimony Is Contradicted By Her Other Opinions

> 54. Second, Dr. Banerjee ignores the disclosures of Stowers 2008 which describe peroxide as being radiation sensitive. For example, in a peroxopolytungstate resist "the mechanism of photoactivity has been shown to be the **decomposition of peroxide groups**." EX1008, 30. Moreover, Stowers 2008 explains that the HafSOx and ZircSOx photoresist materials were adapted from materials "designed as high-k dielectrics." *Id.*, 65. Stowers 2008 adapted those materials by **adding peroxide** to create a radiation sensitive photoresist. *Id.*, 143 (the dielectric materials were adapted to be photoresists by "changing the chemistries to a peroxide based system.") *Compare Id.*, 68 *with* EX1030, 2. It therefore follows that peroxide is the radiation sensitive element of HafSOx and ZircSOx because the peroxide imparts the ability for radiation to act as a photoresist.

EX1040, ¶54

Petitioner's 112 Arguments Fail – Enablement

Petitioner's Enablement Argument Falls With Its WD Argument

- Petitioner's Enablement Argument Relies on Its Written Description Analysis

> Here, the '564 patent's specification does not enable the full scope of the claims, due to the limitation requiring "metal ions with radiation sensitive ligands." Mot. at 6. As identified above in Section III.A.2, the claims cover a combination of "metal ions with radiation sensitive ligands," but the '564 patent provides examples of only two working combinations—hafnium or zirconium ions with hydrogen peroxide ligands. EX1001, 21:12-23:41. By claiming all "metal ions with radiation

Opp., 7

> Similarly, the specification does not enable the full scope of "coating materials" where "radiation alters the chemical properties." Mot. at 6. As explained above in Section **Error! Reference source not found.**, the specification only discloses two coating materials with the claimed functional requirement (i.e., "radiation alters the chemical properties"—namely, coating materials made of hafnium or zirconium with hydrogen peroxide ligands. EX1001, 21:12-23:41. Thus,

Opp., 8

- Petitioner Provides Conclusory Testimony Without Explaining Why "Undue Experimentation." (EX1040, ¶159.)
- No *Wands* Factors Analysis

Petitioner's 112 Arguments Fail – About 25

- **Petitioner applies incorrect *Packard* standard, (Opp., 8-9), not *Nautilus* where the "claims, read in light of the specification delineating the patent, and the prosecution history, fail to inform, with reasonable certainty, those skilled in the art about the scope of the invention."**

Nautilus, Inc. v. Biosig Instruments, Inc., 572 U.S. 898, 901 (2014)

- **Terms of degree are "ubiquitously used in patent claims" without being indefinite.**

Ecolab, Inc. v. Envirochem, Inc., 264 F.3d 1358, 1367 (Fed. Cir. 2001); MPEP § 2173.05(b)

Specification

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. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.

EX1001, 14:55-61

Prosecution History

C) Applicants argue that it is very respectfully submitted that the term "about" is a well-settled term of approximation. Well-established case law shows that a suitable

EX1007, 495

prosecution. Applicant has removed the term "about" from the claims. With respect to the relevant parameters, a person of ordinary skill in the art would interpret "about" in the present context as corresponding to experimental error in the measurements of continuous variable of the present type. From that perspective, the amended claims have effectively the same scope following amendment to remove the term "about" since the values would be interpreted in view of the accuracy of the measurements. In view of the amendment, Applicant respectfully requests

EX1007, 504

Petitioner's Section 112 Arguments Fail – Metal Ions

Petitioner Fails to Prove "Metal Ions" Is Indefinite

Specification Includes Metals and Metalloids

Various metal ions can be provided as metal suboxide cations, such as VO^{+2}, SbO^{+}, ReO_3^{+}, TiO^{+2}, TaO^{+3}, TaO_2^{+}, YO^{+}, NbO^{+2}, MoO^{+2}, WO^{+4}, WO_2^{+2}, AlO^{+}, GaO^{+}, CrO^{+}, FeO^{+}, BiO^{+}, LaO^{+}, CeO^{+}, PrO^{+}, NdO^{+}, PmO^{+}, SmO^{+}, EuO^{+}, GdO^{+}, TbO^{+}, DyO^{+}, HoO^{+}, ErO^{+}, TmO^{+}, YbO^{+}, LuO^{+}, $TiO_y(OH)_z^{(4-2y-z)+}$, $TaO_y(OH)_z^{(5-2y-z)+}$, $YO_y(OH)_z^{(3-2y-z)+}$, $NbO_y(OH)_z^{(4-2y-z)+}$, $MoO_y(OH)_z^{(4-2y-z)+}$, $WO_y(OH)_z^{(6-2y-z)+}$, $AlO_y(OH)_z^{(3-2y-z)+}$, $GaO_y(OH)_z^{(3-2y-z)+}$, $Zn(OH)^{+}$, $CrO_y(OH)_z^{(3-2y-z)+}$, $FeO_y(OH)_z^{(3-2y-z)+}$, $BiO_y(OH)_z^{(3-2y-z)+}$, $LaO_y(OH)_z^{(3-2y-z)+}$, $CeO_y(OH)_z^{(3-2y-z)+}$, $PrO_y(OH)_z^{(3-2y-z)+}$, $NbO_y(OH)_z^{(3-2y-z)+}$, $PmO_y(OH)_z^{(3-2y-z)+}$, $SmO_y(OH)_z^{(3-2y-z)+}$, $EuO_y(OH)_z^{(3-2y-z)+}$, $GdO_y(OH)_z^{(3-2y-z)+}$, $TbO_y(OH)_z^{(3-2y-z)+}$, $DyO_y(OH)_z^{(3-2y-z)+}$, $HoO_y(OH)_z^{(3-2y-z)+}$, $ErO_y(OH)_z^{(3-2y-z)+}$, $TmO_y(OH)_z^{(3-2y-z)+}$, $YbO_y(OH)_z^{(3-2y-z)+}$, $LuO_y(OH)_z^{(3-2y-z)+}$, or combinations thereof. The y and z parameters can be selected such that the ions have a positive charge based on the particular oxidation state of the metal atom. Metal suboxide cations of particular interest include, for example, ZrO^{+2}, $ZrOOH^{+}$, $Zr(OH)_2^{+2}$, $Zr(OH)_3^{+}$, HfO^{+2}, $HfOOH^{+}$, $Hf(OH)_2^{+2}$, $Hf(OH)_3^{+}$ combinations thereof and/or combinations with other metal suboxide cations. Furthermore, the solution can comprise additional metal cations, such as cations of copper, hafnium (Hf^{+4}), titanium (Ti^{+4}), zirconium (Zr^{+4}), cerium (Ce^{+4}), tin (Sn^{+4}), tantalum (Ta^{+5}), niobium (Nb^{+4}), yttrium (Y^{3}), molybdenum (Mo^{+6}), tungsten (W^{+6}), aluminum (Al^{+3}), gallium (Ga^{+3}), zinc (Zn^{+2}), chromium (Cr^{+3}), iron (Fe^{+3}), bismuth (Bi^{+3}), scandium (Sc^{+3}), vanadium (V^{+4}), manganese (Mn^{+2}, Mn^{+3}, Mn^{+4}), cobalt (Co^{+2}, Co^{+3}), nickel (Ni^{+2}, Ni^{+3}), indium (In^{+3}), antimony (Sb^{+5}), iridium (Ir^{+3}, Ir^{+4}), platinum (Pt^{+2}, Pt^{+4}), lanthanum (La^{+3}), praseodymium (Pr^{+3}), neodymium (Nd^{+3}), promethium (Pm^{+3}), samarium (Sm^{+3}), europium (Eu^{+3}), gadolinium (Gd^{+3}), terbium (Tb^{+3}), dysprosium (Dy^{+3}), holmium (Ho^{+3}), erbium (Eb^{+3}), thulium (Tm^{+3}), ytterbium (Yb^{+3}), lutetium (Lu^{+3}) or combinations thereof. As noted above, the state of the cations in solution is pH dependent, such that the initial state of oxygen coordination can change in solution, but the trend is toward hydrolysis leading to oxide formation. It has been found that peroxide-based ligands can hinder the formation of a metal-oxygen network that leads to gelation and ultimately precipitation. Thus, the peroxide can be used to form a stable state that can be quickly condensed upon rupture of the peroxide bonds.

The metal cations generally significantly influence the absorption of radiation. Therefore, the metal cations can be selected based on the desired radiation and absorption cross section. It has been found that ZrO^{+2} provides good absorption of ultraviolet light at 193 nm wavelength and other far ultraviolet radiation. HfO^{+2} provides good absorption of electron beam material and extreme UV radiation. Further tuning of the composition for radiation absorption can be adjusted based on the addition of other metal ions. For example, one or more ions (cations or anions) comprising titanium, zinc, calcium, indium, tin, antimony, bismuth or combinations thereof can be added to the precursor solution to form a coating material with an absorption edge moved to longer wavelengths, to provide, for example, sensitivity to 248 nm wavelength ultraviolet light. Also, one or more ions (cations or anions) comprising magnesium, boron, calcium, aluminum, silicon, phosphorous or combinations thereof can be used to increase the absorption cross section at shorter wavelengths. The energy absorbed is transferred to the peroxide ligand which can result in the rupturing of the peroxide bond, which provides desired control over the material properties.

EX1001, 10:65-11:42

Petitioner Conceded Phosphorous Can Be Metalloid

The specification evidences the patentee's intent to include elements that can be described as metals and metalloids within the term "metal ions," consistent with its plain and ordinary meaning. EX1001, 10:65-11:42. And although Lam points to phosphorous and calls it a "non-metal," Opp., 11; EX1001, 11:35-39, it ignores that phosphorous has been recognized as a metalloid for decades, a fact that Lam conceded at district court (albeit characterizing it as "rare instances"). *Inpria Corp. v. Lam Rsch. Corp.*, Case No. 22-cv-1359-CJB, D.I. 199, pp. 3, 7 (D. Del. Oct. 18, 2024) (joint claim construction brief). The Board should reject Lam's

MTA Reply, 5

Petitioner's Section 112 Arguments Fail – Terms of Degree

Dr. Holland Understood Claims 7 and 12

E. Lam's Arguments That Terms of Degree Are Indefinite Fail

Lam's argument that "high absorption," "conventional radiation-based resists," and "effectively patterned" are indefinite is critically undermined by the fact that its own expert understood each of those terms in attempting to apply the alleged prior art. Opp., 12; EX2011, 130:18-131:15 (effectively pattern); EX2017, 93:7-23 (high absorption), 93:24-94:21, 98:3-12, 101:1-3 (conventional radiation-based resists), 106:25-107:10 (effectively pattern). And Lam's faulting of Dr. Banerjee for not

MTA Reply, 5-6

Petitioner Ignored the Specification

Furthermore, Lam's arguments should be rejected because they ignore the ample context provided for these terms in the '564 patent specification. *E.g.*, EX1001, 1:38-2:13, 2:48-3:2, 4:23-26, 5:23-35, 6:36-47, 8:35-38, 8:67-9:4, 9:57-61, 11:21-42, 19:61-20:3, 20:49-53, Figs. 2-18.

MTA Reply, 6

Petitioner's Section 112 Arguments Fail – *IPXL* Method/Apparatus

Patent Owner's Claims Recite an Apparatus With Particular Capabilities

13. 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 of about 25 nm~~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.

MTA, 13

Petitioner Does Not Apply *IPXL* to the Claims

Reply at 6. This is nonsensical. The premise of a mixed-claim type is that the claim makes it "unclear whether infringement [] occurs when one creates a system…or whether infringement occurs when the user actually" uses the system to perform a method step. *IPXL*, 430 F.3d at 1384. This is exactly the problem here: apparatus

MTA Sur-Reply, 7

F. Lam's *IPXL* Mixed-Claim Type Argument Fails

Lam's reliance on *IPXL Holdings, LLC v. Amazon.com, Inc.*, 430 F.3d 1377, 1384 (Fed. Cir. 2005) is misplaced because Inpria's substitute claims recite "an apparatus with particular capabilities," *UltimatePointer, LLC v. Nintendo Co.*, 816 F.3d 816, 828 (Fed. Cir. 2016), and do not "claim activities performed by the user," *Mastermine Software, Inc. v. Microsoft Corp.*, 874 F.3d 1307, 1316 (Fed. Cir. 2017). Lam's argument as to the "has been heated" limitation lacks any merit and is beyond the pale, as Lam relies on a self-created change of the actual claim language to "heat[ing]" and ignores that Lam itself called this a "structural feature." *Compare* Opp., 13, *with* Reply, 10.

MTA Reply, 6

Petitioner's Stowers 2008 Arguments Fail

- Proposed Amendments
- Motion to Amend Is Compliant
- Petitioner's Section 112 Arguments Fail
- **Petitioner's Section 102 and 103 Arguments Fail**
  - **Petitioner's Stowers 2008 Arguments Fail**
  - Petitioner's Trikeriotis Arguments Fail
  - Petitioner's Keszler Arguments Fail

Claim 13 – Petitioner's Stowers 2008 Arguments Fail

Petitioner's Arguments Fail for About 25 nm

Stowers 2008 Background

Work in direct patterning was initiated after the development of the thin-film chemistry of the material HafSOx [1]. HafSOx is an aqueous solution-deposited material based on various compositions of hafnium oxide sulfate that was initially designed as a high-k dielectric. HafSOx, and its zirconium analog ZircSOX, can be deposited in films ranging in thickness from 2 to 500 nm. The films are characterized by being atomically smooth surfaces. Taken together, these properties serve as an excellent starting point for the development of a directly patterned metal oxide. Furthermore, with the proper patterning characteristics this material could be adapted as a high quality inorganic resist.

EX1008, 18

Stowers 2008 Example 3

Substrates were either silicon wafer chips (n^+ heavily doped) or silicon coupons with 200 nm of thermal oxide. The substrates for UV exposure were prepared for spincoating by sonication in Decon Labs, Contrad 70 at 45°C for 60 min. Substrates for EUV exposure were prepared by immersion in a fresh piranha etch solution (3 parts H_2SO_4 to 2 parts H_2O_2) for 1 min. Working solutions were spin coated at 3000 rpm for 30 seconds resulting in films 30 to 35-nm thick.

EX1008, 68

Claim 13 – Petitioner's Stowers 2008 Arguments Fail

Petitioner's Arguments Fail for About 25 nm

Petitioner Provides No Analysis for Pattern Collapse to Reduce Stowers 2008's 30 nm Films to 25 nm

> EX1008 at 18. While this range is dispositive, a POSA also would have been motivated to reduce Stowers 2008's 30 nm thickness to avoid pattern collapse (EX1009, 265 ("Stowers [2008] described coatings with thicknesses from 30 to 35 nm in Chapter 3.")); EX1040, ¶¶130-132; EX1012, 8. Accordingly, it would have been obvious to reduce the 30 nm thickness disclosed in Stowers 2008 to 25 nm to reduce pattern collapse. EX1040, ¶¶130-132. Substitute claim 13 is therefore not patentable over Stowers 2008.

Opp., 15

Claim 19 – Petitioner's Stowers 2008 Arguments Fail

Petitioner's Arguments Fail For Radiation Sensitive Ligand Ratio

Stowers 2008 Discloses Different Ratio

combined to produce a working solution which were directly spin coated. Working solutions 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

EX1008, 68

Petitioner Relies on Stowers 2008 Conclusions

In Chapter 3, the patterning of HafSOx and ZircSOx was significantly improved on by changing chemistries to a peroxide based system. Sensitivity to UV ($\lambda <$ 254nm) and EUV light was demonstrated. The contrast of the unoptimized photolithographic process was generally found to be low. In the future, photolithography deserves revisiting using the knowledge gained using electron-beam lithography.

EX1008, 143

Dr. Holland Relies on Hindsight

137. Indeed, this is precisely what Stowers later did. EX1019, 4. Stowers discovered that at ratios higher than those in the Stowers 2008 films, the concentration saturates, and the remaining peroxide is unbound. *Id.* This study showed the differences in peroxide to metal ratios in HafSOx resist materials. *Id.* As discussed above, EX1019 shows that that for peroxide to metal ratios less than 0.5 "all of the peroxide coordinates to the [hafnium] clusters." *Id.* However, when the ratio "exceeds 0.5, the free peroxide stretching mode … appears while the bound peroxide saturates in intensity" which "suggests that approximately two peroxide groups coordinate to each hafnium tetramer." *Id.*

EX1040, ¶137

Petitioner's Trikeriotis Arguments Fail

- Proposed Amendments
- Motion to Amend Is Compliant
- Petitioner's Section 112 Arguments Fail
- **Petitioner's Section 102 and 103 Arguments Fail**
  - Petitioner's Stowers 2008 Arguments Fail
  - **Petitioner's Trikeriotis Arguments Fail**
  - Petitioner's Keszler Arguments Fail

Petitioner's Trikeriotis Arguments Fail

Lam Argues "Taught By Trikeriotis" But Identifies No Express Teachings for About 25 nm

Proposed Amended Claim 13 (substitute for Claim 1)

13. 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 of about 25 nm~~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.

MTA, 13

Trikeriotis discloses that "film thicknesses ranging from 30 nm to 200 nm can be easily achieved." EX1024, 18. Inpria cherry picks out of context statements from

Opp., 16

Petitioner's Trikeriotis Arguments Fail

Lam Relies on Generalized Statements While Ignoring Trikeriotis's "Thicker Films"

ABSTRACT

The trend of ever decreasing feature sizes in subsequent lithography generations is paralleled by the need to reduce resist thickness to prevent pattern collapse. Thinner films limit the ability to transfer the pattern to the substrate during etch steps, obviating the need for a hardmask layer and thus increasing processing costs. For the 22 nm node, the critical aspect ratio will be less than 2:1, meaning 40-45 nm thick resists will be commonplace. To address this problem, we have developed new inorganic nanocomposite photoresists with significantly higher etch resistance than the usual polymer-based photoresists. Hafnium oxide nanoparticles are used as a core to build the inorganic nanocomposite into an

EX1024, 15

film. The film that was used was only 30 nm thick to minimize the absorbance and reflection of light. Currently, optimization of the photoresist formulation is underway to pattern 60 nm features on thicker films.

EX1024, 21

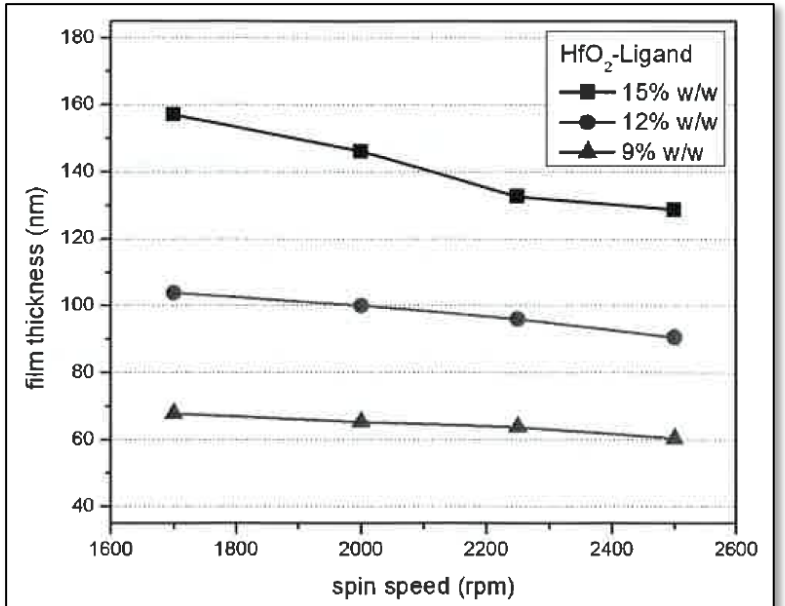


Figure 3. Film thickness versus spin speed at different nanoparticle loadings

EX1024, 18 (Fig. 3)

Petitioner's Trikeriotis Arguments Fail

New Sur-Reply Argument for "Future Feature Sizes"

to prevent pattern collapse." EX1024, 15. While Trikeriotis believed that current needs could be solved by using films from 30 nm thick, the unrebutted testimony from Dr. Holland confirms that a POSA would be motivated to prepare for ***future*** feature size needs by reducing thickness to "about 25 nm." EX1040, ¶¶133-134. And

MTA Sur-Reply, 10-11

Dr. Holland Never Mentions "Future Feature Sizes"

b. It would have been obvious modify the coatings of Trikeriotis to have a thickness of about 25 nm

133. Trikeriotis discloses that "film thicknesses ranging from 30 nm to 200 nm can be easily achieved." EX1024, 18. Although Trikeriotis was testing a variety of film thicknesses, including those thicker than 30 nm, Trikeriotis explained that "[t]he trend of ever decreasing feature sizes in subsequent lithography generations is paralleled by the need to reduce resist thickness to prevent pattern collapse." EX1024, 15. This is consistent with a POSA's understand that film thickness should be reduced to avoid pattern collapse. *E.g.*, EX1012, 8 ("pattern collapse depends on the pattern height"). Accordingly, as discussed above a POSA would have recognized that film thickness is a variable that a POSA would have been motivated to optimize.

134. Given the ease with which film thickness can be varied, *e.g.*, by adjusting spin rates and times (EX1008, 6; EX1001, 14:30-32), finding an optimum thickness range to mitigate pattern collapse would have required nothing more than routine experimentation. Indeed, Dr. Banerjee stated during his deposition that optimizing the thickness "is not rocket science[,] [i]t's not extensive experimentation by any means." EX1033, 75:5-11. Thus, a POSA could have easily deposited the claimed coatings at a thickness of about 25 nm based on the teachings of Stowers 2008 with routine experimentation.

EX1040, ¶¶133-134

Petitioner's Keszler Arguments Fail

- Proposed Amendments
- Motion to Amend Is Compliant
- Petitioner's Section 112 Arguments Fail
- **Petitioner's Section 102 and 103 Arguments Fail**
  - Petitioner's Stowers 2008 Arguments Fail
  - Petitioner's Trikeriotis Arguments Fail
  - **Petitioner's Keszler Arguments Fail**

Petitioner's Keszler Arguments Fail

Petitioner Argues Keszler Anticipates Claims 13-18 and 20-23 and Renders Obvious Claim 19

V. PROPOSED AMENDED CLAIMS 13-18 AND 20-23 ARE ANTICIPATED BY KESZLER (EX1038) AND PROPOSED AMENDED CLAIM 19 IS RENDERED OBVIOUS BY KESZLER (NEW GROUNDS).

Keszler published on July 10, 2008. EX1038, 1. Keszler is therefore prior art to the '564 patent under pre-AIA §102(b). Keszler is an International Application Publication which names Oregon State University as an applicant and names Doulas Keszler, Jason Stowers (who are each inventors of the '564 patent), Jeremy Anderson, Peter Hersh, and Stephen Meyers as inventors. *Id.* Keszler discloses hafnium or zirconium films, which it refers to as HafSOx or ZircSOx. *Id.*, 5:4-9. Keszler explains that the hafnium or zirconium oxy hydroxy compounds can be used in a photoresist layer for patterning a device. *Id*, 6:16-25. As shown in detail below, Keszler discloses each and every limitation of (and therefore anticipates) proposed amended claims 13-18 and 2-23 and renders obvious proposed amended claim 19.

Opp., 17

MTA Reply, 10-11

Petitioner's Keszler Arguments Fail – Claim 13

Petitioner Improperly Cites Various, Distinct Embodiments in Keszler for Anticipation

- **"[A]nticipation is not proven by multiple, distinct teachings that the artisan might somehow combine to achieve the claimed invention."**

Microsoft Corp. v. Biscotti, Inc., 878 F.3d 1052, 1069 (Fed. Cir. 2017).

A. Independent Claim 13

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

Keszler discloses "patterning a device using a photoresist" by "providing a **structure**" which comprises a "resist layer." EX1038, 4:16-25. Example 4 of Keszler discloses that "thin **films** were deposited on **silica substrates**" by spin coating precursor solutions onto the substrate. *Id.*, 40:8-20. Similarly, Example 7 disclose "**inorganic film** containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto **an appropriate substrate**." *Id.*, 42:8-10. A POSA would have understood that the films are "coatings" on the surface of a "substrate." EX1040, ¶¶90-91. Keszler therefore discloses the preamble.

2. "coating material comprises metal ions with radiation sensitive ligands"

Keszler discloses that the "resist layer typically includes disclosed **hafnium** and/or **zirconium** oxy hydroxy compounds." EX1038, 4:16-25. In Example 4, Keszler discloses precursor solutions comprising hafnium ("Hf") or zirconium ("Zr") ions and peroxide ("H_2O_2") ligands. *Id.*, 38:6-63. Consistent with Keszler's

Opp., 17-18

Example 4 is a radiation sensitive ligand. EX1038, 28:9-12. A POSA would understand that the hydrogen peroxide (H_2O_2) of the precursor solutions of Keszler Example 4 are "peroxide" ($O2^{2-}$) and that because inclusion of the peroxide into the precursor solutions provides a "new lithographic patterning method," the peroxides are "radiation sensitive ligands." EX1040, ¶96. Because the precursor solutions in

3. "coating material has an average thickness of about 25 nm"

Keszler discloses depositing the precursor solutions as "a thin film (from about 1 nm to about 100 nm)." EX1038, 32:3-15. For example, Example 4's precursor solutions can produce "films as thin as about 2 nm." *Id.* 40:1-2. Indeed, by

Opp., 19

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"

Keszler discloses that that patterns are formed by changing the chemical structure of the resist layer via radiation, which creates a coating material with differential dissolution rates between exposed and un-exposed regions:

> Patterns can be formed using a positive or negative photoresist…For positive resists, the resist layer 1016 is **exposed** to an energy source, such as **UV** light, wherever the underlying material is to be removed. In these resists, exposure to the UV light **changes the chemical structure** of the resist layer 1016 so that it becomes **more soluble**….

Id. 28:15-21; *see also id.* at 8:1-12.

Opp., 20

MTA Reply, 10-11

Petitioner's Keszler Arguments Fail – Claim 13

Petitioner Improperly Cites Various, Distinct Embodiments in Keszler for Anticipation

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 °C for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

EX1038, 40:7-23

Example 7

This example describes general methods for patterning a single-layer inorganic film. A single inorganic film containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto an appropriate substrate. The film is heated at modest temperatures of less than 100°C to provide structural integrity to the film. The film is then exposed through a photomask to high-energy light, a maskless pattern via spatial light modulation, a defined laser beam, or electron beam to define a pattern or other preferred film features. Two examples of photogryaphically patterned films are shown in FIGS. 33 and 34. FIG. 33 is a patterned $ZrO_{2-x}(SO_4)_x$ film. FIG. 34 is a patterned TiO_2 film. The TiO_2 film was about 15-50 nm thick. It was patterned using an unfiltered deuterium lamp, followed by etching with 0.1-0.2 M HCl for less than 60 seconds. FIGS. 35-37 are $HfO_{2-x}(SO_4)_x$ films patterned by an electron beam. The films were about 30-60 nm thick. They were patterned using an electron beam at a dose level of 200 $\mu C/cm^2$, followed by etching with 5-12 M HCl for about 1-4 minutes.

EX1038, 44:7-27

Petitioner's Keszler Arguments Fail – Claim 13

Petitioner Improperly Cites Various, Distinct Embodiments in Keszler for Anticipation

During the deposition and processing of the films described herein, it is possible to control the film hydration level, which provides a method for controlling the interdiffusion of stacked films and their resulting physical and chemical properties. This controlled interdiffusion with resulting induced modifications in material solubility, coupled with the high quality of the films, was used to develop a new lithographic patterning method. This methodology involves depositing and reacting two distinct films, and it is designated as bilayer diffusion. In addition, small coordinating species such as peroxide (O_2^{2-}) can be incorporated into aqueous-based inorganic liquid suspensions and films to provide an additional, new lithographic patterning method. In this technique, energy (e.g., light, electron beam, heat) can be applied to films, inducing condensation reactions that alter the solubility of the film, thereby allowing lithographic patterning.

Patterns can be formed using a positive or negative photoresist. This process is illustrated schematically in FIG. 10 with reference to a laminate structure 1010 having a silicon substrate 1012, a silica layer 1014 and a resist layer 1016. For positive resists, the resist layer 1016 is exposed to an energy source, such as UV light, wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist layer 1016 so that it becomes more soluble in the developer. The exposed resist layer 1016 is then

EX1038, 28:4-21

Example 6

This example describes two general methods of bilayer inorganic lithographic processing. In one working embodiment, a HafSOx film with a thickness from about 30 nm to about 60 nm was solution deposited onto a SiO_2/Si substrate. The substrate was placed directly onto a hot-plate set at about 50 °C and heated to impart structural integrity to the film. The resulting film was acid insoluble. The substrate was then placed on a heated platen (about 50 °C to 200 °C) of an ink-jet printer, where copper formate lines were printed onto the substrate via a thermal ink-jet head. Copper formate decomposed and diffused into the HafSOx film on heating, rendering the film soluble. Following a rinse in water, additional heating to about 300 °C, and development in dilute acid, the drawn lines were clearly evident as shown in FIG. 29.

EX1038, 43:15-26

Petitioner's Keszler Arguments Fail – Claim 13

Petitioner Relies on Same Faulty "Same Components" Inherency Argument

> Moreover, the Keszler Example 4 precursor solutions contain the same components as the precursor solutions used to make the coating materials in the Examples of the '564 patent (i.e., $HfOCl_2$ or $ZrOCl_2$, H_2O_2 and H_2SO_4) and other publications discussing the photosensitivity of the peroxide ligands in HafSOx and ZircSOx. EX1040, ¶¶97-100. Any differences in the precursor solutions or processing conditions are immaterial. *Id.* Accordingly, because the '564 patent and other post-priority publications describe that the peroxide in the precursor solution is a radiation sensitive ligand (i.e., an inherent property of the material), EX1001, 6:9-10, the peroxide in the precursor solution of Keszler is also a radiation sensitive ligand. *See Alcon Rsch., Ltd. v. Apotex Inc.*, 687 F.3d 1362, 1369 (Fed. Cir. 2012) (analyzing inherency based on the disclosure of the "patent itself").

Opp., 19

Petitioner's Keszler Arguments Fail – Claim 13

Petitioner Does Not Prove Keszler's Example 4 Films Are the Same as the '564 Patent Films

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 ºC for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

EX1038, 40:7-23

	'564 Patent
Metal Concentration	0.16 M (Zr) 0.15 M (Hf) EX1001, 21:59, 64
Rests	5 minute rests after each addition. EX1001, 21:23-55
Pre-exposure bake	40-200° C for 0.1-5 minutes 50° C EX1001, 22:20-21, 23:36-37.
Post-exposure bake	40-200° C for 1-5 minutes 75° C EX1001, 22:43, 23:38
Spin coating conditions	100 RPM for 5 seconds and then 3000 RPM for 30-60 seconds EX1001, 22:17-20
Substrate	Five inch silicon wafers EX1001, 22:7
Metal to peroxide ratio	1 to 0.66-0.88 (Zr) 1 to 6.62-8.81 (Hf) EX1002, ¶38 (calculations based on EX1001, 21:10-67 (Example 1)); POPR, 29 n.4 (noting the error in the calculations); EX2011, 123:6-124:12 (Dr. Holland admitting the error).[9]

POR, 33-34; MTA Reply 10-11

Petitioner's Keszler Arguments Fail – Claim 18

Petitioner Relies on "Same Films," Density Inherency, and a 2011 Document for EUV Absorption

Claim 18: Proposed claim 18 depends on claim 13 and recites that the "coating material has high absorption of EUV radiation relative to conventional radiation-based resists." The HafSOx and ZircSOx films are materially the same as those in the '564 patent. EX1040, ¶¶97-100, 116. Thus, Keszler's HafSOx films must necessarily have "high absorption of EUV radiation relative to conventional radiation-based resists," per the '564 patent. EX1001, 8:67-9:2,11:26-27.

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Moreover, a publication by Jason Stowers and Douglas Keszler (inventors of both Keszler and the '564 patent) reports that metal oxide sulfate (MSOx), such as HafSOx and ZircSOx, have 4-x more EUV absorption compared to "conventional polyhydroxystyrene" resists. EX1022, 3; EX1040, ¶114. This is consistent with reports that EUV absorption increases with density of materials. EX1025, 4; EX1002, ¶136; *see also* EX1040, ¶¶115-116. Thus, HafSOx and ZircSOx would

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Petitioner Fails to Link Keszler Films to Exhibit 1022's "Current Generation" Films

For 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. 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/cm^3. This mass density and the compositional information are used to calculate EUV absorption from the Center for X-Ray Optics database,[11] 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 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.

EX1022, 3

Petitioner's Keszler Arguments Fail – Claim 19

Petitioner's Conclusory "Optimize" Argument for Radiation Sensitive Ligand Ratio

Claim 19: Proposed claim 19 depends on claim 13 and recites that the structure has a "molar concentration ratio of radiation sensitive ligands to metal ion of at least 2." Keszler discloses a precursor solution comprising $HfOCl_2$ or $ZrOCl_2$, with H_2O_2 and H_2SO_4 to form photoresists. EX1038, 32:14-15. Keszler Example 4's precursor solution comprises a molar concentration ratio of ligand to metal of 0.7:1. EX1040, ¶125. Keszler discloses that the peroxide allows the films to act as photoresists. EX1038, 28:9-12 (inclusion of peroxide provides a "new lithographic patterning method."); EX1040, ¶126. The peroxide content of the films is therefore a result-effective variable that a POSA would modify to optimize the sensitivity of the film. EX1040, ¶¶135-138. The optimization of the result-effective peroxide content is "within the grasp" of a POSA. *Applied Materials*, 692 F.3d at 1296; *see also* Pfizer, 94 F.4th at 1347-48; *Aller*, 220 F.2d at 456.

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Petitioner's Keszler Arguments Fail – Claim 23

Petitioner Relies on No Pattern for "Effective Patterning"

at a dose of no more than 100 mJ/cm^2." Keszler discloses that the HafSOx materials were patterned with an "electron beam at dose levels ranging from greater than 0 μC/cm^2 to at least 400 μC/cm^2" and could be patterned as "at dose levels as low as 2 μC/cm^2." EX1038, 33:13-18. A dose of 2 μC/cm^2 corresponds to a UV radiation or EUV radiation at a dose of no more than 100 mJ/cm^2 as confirmed by the '564 patent (EX1001, ("The method can comprise irradiating a layer of coating material

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dimensions. FIG. 16 is an AFM (atomic force microscope) image of a HafSOx film patterned via a single-layer, negative tone process with an electron beam at dose levels ranging from greater than 0 μC/cm^2 to at least 400 μC/cm^2. The nanometer scale to the right of the image indicates the height of the features etched into the film. As shown in FIG. 16, features have been written via electron-beam exposure at dose levels as low as 2 μC/cm^2. This dose level is comparable to the best known

EX1038, 33:13-18

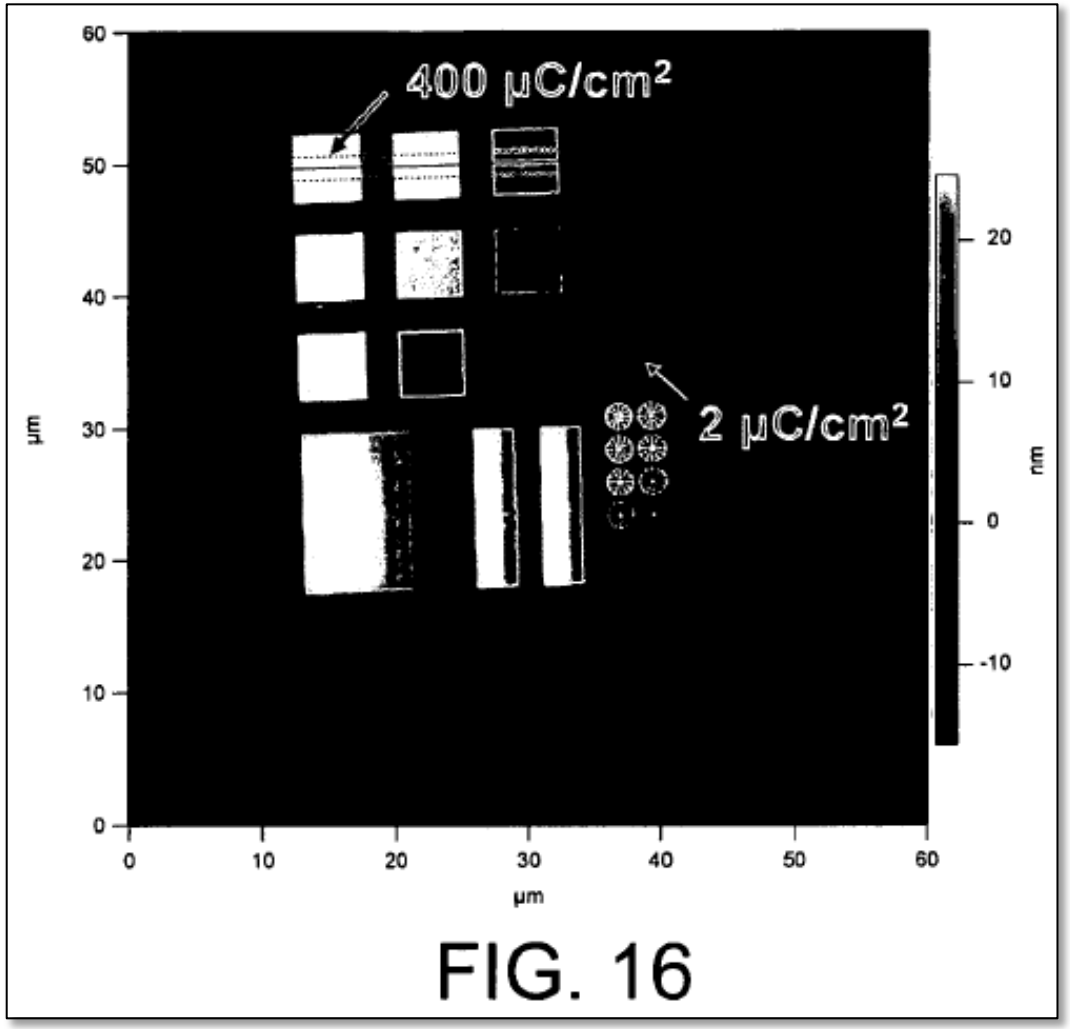


FIG. 16

EX1038, 60 (Fig. 16)

MTA Reply, 11-12

Patent Owner Demonstratives

United States Patent and Trademark Office
Before the Patent Trial and Appeal Board

Lam Research Corp., Petitioner v. Inpria Corp., Patent Owner

U.S. Patent No. 9,823,564

Case: IPR2024-00033

Oral Hearing: January 30, 2025