

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

LAM RESEARCH CORP.,
Petitioner

v.

INPRIA CORP.,
Patent Owner

Case IPR2024-00033
Patent No. 9,823,564

**DECLARATION OF SANJAY BANERJEE, PH.D.
IN SUPPORT OF PATENT OWNER'S RESPONSE**

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I, Sanjay Banerjee, Ph.D., declare as follows:

I. INTRODUCTION

1. I have been retained by Inpria Corporation (“Patent Owner”) as an independent expert consultant in this proceeding before the United States Patent and Trademark Office (“PTO”) involving U.S. Patent No. 9,823,564 (“the ’564 patent”) (EX1001). I have been asked to consider whether a person of ordinary skill in the art would have understood the inventors of the ’564 patent to be in possession of certain features recited in the claims of the ’564 patent. I have also been asked to provide opinions relating the formation of resist films and relating to the possible changes to materials based on exposure to ultraviolet (UV) or extreme ultraviolet (EUV) radiation, as well as certain scientific theories presented by Lam Research Corporation (“Lam”). My opinions are set forth below.

2. I am being compensated at my customary rate for my work in this proceeding. My compensation is in no way contingent on the nature of my findings, the presentation of my findings in testimony, or the outcome of this or any other proceeding. I have no other interest in this proceeding.

II. BACKGROUND AND QUALIFICATIONS

3. I am an independent consultant. All of the opinions stated in this declaration are based on my own personal knowledge and professional judgment. In

forming my opinions, I have relied on my knowledge and experience in researching and teaching aspects of semiconductor technology, as referenced in this declaration.

4. I am over the age of 18 years and, if I called upon, I am competent to testify regarding the matters herein. I understand that a copy of my current curriculum vitae, with details of my education, professional, and academic experience, is attached as Exhibit 2010. The following text is a summary of some of my experiences relevant to the matters set forth in this declaration.

5. I am currently the Cockrell Family Chair Professor of Electrical and Computer Engineering at the University of Texas at Austin. At UT Austin, I am also the director of the Microelectronics Research Center. I have been a faculty member at UT Austin since 1987.

6. I have also been active in industries related to the relevant field of art. As a Member of the Technical Staff, Corporate Research, Development and Engineering of Texas Instruments Incorporated from 1983-1987, I worked on polysilicon transistors and dynamic random access trench memory cells used by Texas Instruments in the world's first 4-Megabit CMOS DRAM, for which I was co-recipient of the Best Paper Award, IEEE International Solid State Circuits Conference, 1986.

7. I received a B. Tech from the Indian Institute of Technology, Kharagpur, and an M.S. and Ph.D. from the University of Illinois at Urbana-Champaign, all in Electrical Engineering.

8. I am a leading researcher and educator in various areas of metal oxide semiconductor field effect transistor (MOSFET) device fabrication technology, including the fabrication, characterization and applications of memory devices, transistors, and nanotechnology. My research has been funded by the Texas Advanced Technology Program (ATP), the Texas Higher Education Coordinating Board, the National Science Foundation, the SEMATECH (Semiconductor Manufacturing Technology) consortium, the SRC (Semiconductor Research Corporation) consortium, DARPA, and the Department of Energy, among others. I also previously served as the director of the South West Academy of Nanoelectronics, one of three centers in the United States to develop a replacement for MOSFETs.

9. I have published over 1,200 technical articles, and 35 patents many related to integrated circuits and semiconductor fabrication technology, most at highly competitive refereed conferences and rigorously reviewed journals. I have used photolithography and electron beam lithography in my research for over 40 years. My lab has two electron beam lithography tools, as well as UV mask aligners. We use many different types of photoresists and e-beam resists in my group. As part

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of my collaboration with industry (e.g. SEMATECH), I have used UV steppers. I have also taught a graduate course on Microelectronic Fabrication where my students make transistors. In the lectures, I discuss photoresist chemistry, photoresist processing including baking, exposure and development. I also discuss UV, EUV and Electron Beam Lithography. I have also published 10 books or chapters on transistor device physics and fabrication, and have supervised over 80 Ph.D. and 60 MS students. My publications are listed at: <http://banerjeelab.mer.utexas.edu/>.

10. I have been a member of scientific organizations and committees, including the IEEE Dan Noble Award Committee from 2010-2013, serving as Chair from 2012-2013, the International Technology Roadmap for Semiconductors, the International Conference on MEMS (Microelectromechanical Systems) and Nanotechnology, the IEEE International Conference on Communications, Computers, Devices, the International Electron Devices Meeting, the International Conference on Simulation of Semiconductor Processes and Devices, and the IEEE Symposium on VLSI (Very-Large-Scale Integration) Technology.

11. I have served as the Session Chair for the “Device Technology” Session conducted at the IEEE International Electron Devices Meeting in 1989-1990. I have also served as the General Chairman for the IEEE University Government Industry Microelectronics Symposium in 1994-1995, and Chair of the IEEE Device Research Conference.

12. I have served on the Technical Advisory Boards of Applied Novel Devices, Graph Audio, AstroWatt, DSM Semiconductors, Cambrios, Nanocoolers Inc., BeSang Memories, Organic ID and ITU Ventures; Gerson Lehmann Group, NY; Austin Community College; Asia Pacific IIT; Rochester Institute of Technology, and HSMC Foundry.

13. I received the Engineering Foundation Advisory Council Halliburton Award (1991), the Texas Atomic Energy Fellowship (1990-1997), Cullen Professorship (1997-2001) and the Hocott Research Award from UT Austin (2007). I also received the IEEE Grove Award (2014), Distinguished Alumnus Award, IIT (2005), Industrial R&D 100 Award (2004), ECS Callinan Award, 2003, IEEE Millennium Medal (2000), NSF Presidential Young Investigator Award (1988), and several SRC Inventor Recognition and IEEE Best Paper Awards.

14. I was a Distinguished Lecturer for IEEE Electron Devices Society, and am a Fellow of the Institute of the Electrical and Electronics Engineers (IEEE), the American Physical Society (APS) and the American Association for the Advancement of Science (AAAS). I was elected a Fellow of the National Academy of Inventors in 2021.

15. Additional details about my employment history, fields of expertise, awards, publications, and other activities are further included in my curriculum vitae, attached as Exhibit 2010.

III. MATERIALS REVIEWED

16. The opinions contained in this Declaration are based on the documents I reviewed, my professional judgment, as well as my education, experience, and knowledge regarding semiconductor processing, including lithography and photoresist materials used to pattern semiconductor devices.

17. In forming my opinions expressed in this Declaration, I reviewed the following materials and information: U.S. Patent 9,823,564 (EX1001); Holland Declaration (EX1002); the file history for U.S. Patent Application 12/850,867 (EX1004); Stowers 2008 (EX1008); Trikeriotis (EX1024); McCloy Declaration (EX2001);¹ U.S. Patent No. 6,987,572 (EX2005); U.S. Patent No. 7,220,531 (EX2006); and Seong-Yun Moon, Jong-Man Kim, *Chemistry of photolithographic imaging materials based on the chemical amplification concept*, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 8 (2007) 157-173 (“Moon”) (EX2007). I also reviewed any other materials I refer to in this Declaration in support of my opinions.

18. My opinions contained in this declaration are based on the documents I reviewed and my knowledge and professional judgment. My opinions have also

¹ I generally agree with the opinions expressed by Dr. McCloy in his declaration and portions of his analysis are adopted as my own in this declaration, where relevant.

been guided by my appreciation of how a person of ordinary skill in the art would have understood the state of the art, the prior art, and the claims and the specification of the '564 patent at the time of the invention.

19. I understand that the '564 patent issued from U.S. Patent Application No. 14/858,612 ("the '612 application") filed on September 18, 2015, and claims priority to U.S. Patent Application No. 12/850,867 ("the '867 application") filed on August 5, 2010, and Provisional Patent Application No. 61/350,103 ("the '103 provisional") filed on June 1, 2010. (EX1001, Cover.) For purposes of rendering my opinions, I have been asked to initially consider that the time of the invention of the '564 patent is around June 1, 2010 to August 5, 2010. My opinions reflect how one of ordinary skill in the art (which I described below) would have understood the '564 patent and the state of the art at the time of the invention as I was asked to consider noted above.

IV. PERSON OF ORDINARY SKILL IN THE ART AT THE TIME OF THE INVENTION

20. For purposes of this declaration, I have been asked to assume Dr. Holland's definition of a person of ordinary skill in the art. Dr. Holland states her opinion that a person of ordinary skill in the art is an individual with at least a graduate degree, such as a masters or Ph.D., in a relevant discipline such as in chemistry, materials science, chemical engineering, physics, or an equivalent field.

(EX1002, ¶20.) Dr. Holland further testified that such a person of ordinary skill in the art would have 1-3 years of experience in the research, design, development and/or testing of resist materials. (EX1002, ¶20.)

21. Based on my knowledge and experience, I understand what such a person of ordinary skill in the art would have known at the time of the alleged invention. All of my opinions in this declaration are from the perspective of one of ordinary skill in the art, during the relevant timeframe (e.g., the time of the invention), which I discussed above as being around June 1, 2010 to August 5, 2010.

V. CLAIM CONSTRUCTION

22. I understand that claim terms are typically given their ordinary and customary meanings, as would have been understood by a person of ordinary skill in the art at the time of the alleged invention. I have been asked to apply the plain and ordinary meaning of the terms in those claims. I understand that in considering the meaning of the claims, one must consider the language of the claims, the specification, and the prosecution history of record. I have done so to support my opinions in this petition where appropriate.

VI. DISCLOSURE OF THE '867 APPLICATION

23. I have been asked to review and consider whether a person of ordinary skill in the art would have understood, based on the disclosure of the '867 application, that the inventors of the '564 patent were in possession of a certain

element of claim 1, namely the recited average thickness range of 5 nm to 30 nm for the coating material. As detailed below, in my opinion, based on the disclosure of the '867 application, such a person of ordinary skill in the art would have understood the inventors had possession of the invention recited in claim 1, including the 5 nm to 30 nm average thickness range.

24. The '867 application discloses depositing a coating material on the surface of a substrate and further details the process by which such depositing can be accomplished. (EX1004, 22:21-24:21.)² The '867 application notes that “[i]f patterning is performed using radiation, spin coating can be a desirable approach to cover the substrate relatively uniformly, although there can be edge effects.” (EX1004, 23:1-2.) In addition to spin coating, the '867 application also discloses other techniques for depositing the coating material. (EX1004, 22:21-27.)

25. In the context of spin coating, the '867 application explains that “[t]he thickness of the coating generally can be a function of the precursor solution concentration, viscosity and the spin speed.” (EX1004, 23:14-15.) With respect to

² These citations to EX1004 are to the '867 application that spans pages 3-51 of EX1004. As a result, the page numbers for the exhibit are offset from the pages of the patent application by two. For example, page 22 of EX1004 corresponds to page 20 of the '867 application.

spin speed of the wafer during spin coating, the '867 application provides certain example spin speeds:

In some embodiments, a wafer can be spun at rates from about 500 rpm to about 10,000 rpm, in further embodiments from about 1000 rpm to about 7500 rpm and in additional embodiments from about 200 rpm to about 600 rpm. **The spinning speed can be adjusted to obtain a desired thickness.**

(EX1004, 23:3-6 (emphasis added).)

26. Aside from spin coating, the '867 application discloses that “[f]or other coating processes, the thickness can generally also be adjusted through the selection of the coating parameters.” (EX1004, 23:15-16.) The '867 application also describes controlling the thickness of the coating by applying the coating material in multiple coating steps. (EX1004, 22:27-30 (“The coating material can be applied in multiple coating steps to provide greater control over the coating process. For example, **multiple spin coatings can be performed to yield an ultimate coating thickness desired.**”) (emphasis added).) The importance and desirability of certain thicknesses or thickness ranges is further supported by the '867 application's explanation as to how such thicknesses can be measured. (EX1004, 23:24-26 (“The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.”).)

27. The '867 application explains that “it can be desirable to use a thin coating to facilitate formation of small and highly resolved features” (EX1004, 23:16-18), where specific example thickness ranges are provided:

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.

(EX1004, 23:18-22.) While providing these example thickness ranges, the '867 application states that “[a] person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit ranges above are contemplated and are within the present disclosure.” (EX1004, 23:22-24.) The '867 application also discloses an example in which the “coating material was deposited at a thickness [from] 10-50 nm,” (EX1004, 35:14-15) and an example where the “resist was applied with a thickness of 20nm” (EX1004, 36:29-30).

28. Notably, many of the example ranges (“no more than about 1 micron,” “no more than about 250 nanometers (nm),” “about 1 nanometers (nm) to about 50 nm,” and “about 1 nm to about 40 nm”) include the claimed range. In addition, both

of the “1 nm to 25 nm” and “10-50 nm” ranges overlap the claimed range, and the example thickness of 20 nm falls within the claimed range.

29. In my opinion, based on the description of the '867 application, a person of ordinary skill in the art would have immediately discerned that the inventors possessed the claimed range of 5 nm to 30 nm. As I discuss above, the inventors provided example ranges that include the claimed range and explained how various thicknesses can be achieved. Moreover, the inventors explicitly stated that “[a] person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit ranges above are contemplated and are within the present disclosure.” (EX1004, 23:22-24.) I agree with this statement in the specification, as the details and examples provided convey to a person of ordinary skill in the art that additional ranges within those example ranges are within the disclosure of the '867 application. Therefore, such a person of ordinary skill in the art would have further understood that the inventors were in possession of those additional ranges, including the range of 5 nm to 30 nm.

VII. IMPACT OF DIFFERENCES IN RATIOS AND CONCENTRATIONS OF MATERIALS AND PROCESSING CONDITIONS ON RESULTING FILMS

30. I have been asked to consider, in the context of films such as those discussed in the '564 patent, whether differences in the ratios/concentrations of materials and differences in the manner in which those materials are combined can

have an impact on the resulting film produced. As I explain below, a person of ordinary skill in the art would have understood that differences in the ratios and concentrations of materials used to form coating layers, as well as differences in the manner in which those materials are combined, can result in coating films with different characteristics.

31. As one example, the '564 patent teaches that higher ratios of peroxide to metal in the precursor solutions used to produce the coating films can provide advantages, including improved stability of the precursor material:

The precursor solutions have been formulated with improved stability and control of the precipitation so that radiation can be used to induce a change in the material. *In particular, peroxide-based ligands stabilize the precursor solutions while also providing control over the processing of the materials.*

Specifically, the precursor solution can comprise sufficient radiation sensitive ligands such that the solution has a molar concentration ratio of radiation sensitive ligands to metal suboxide cations of at least about 2 and in some embodiments at least about 5. *In particular, the higher peroxide-based ligand concentrations provide for a surprisingly large improvement in the precursor stability. While not wanting to be limited by theory, the increase in the radiation sensitive ligand concentration*

evidently reduces agglomeration of the metal cations to stabilize the solution. Thus the precursor solution can be stable relative to settling of solids without further stirring for at least two hours and possibly for significant longer periods of time, such as greater than a month. Due to the long stability times, the improved precursors have increased versatility with respect to potential commercial uses. Hydrogen peroxide provides a desirable radiation sensitive ligand, although other inorganic peroxides can be suitable.

(EX1001, 5:55-6:11 (emphasis added); *see also* EX1001, 13:11-14 (“As noted above, a relatively large ratio of peroxide-based ligand relative to the metal cations can be used to greatly stabilize the precursor solutions.”).)

32. In addition to the ratio of peroxide ligands to metal of at least about 2 and 5 above, the '564 patent further discloses other ratios where the peroxide is much higher in concentration than the metal:

The precursor composition generally comprises a ligand concentration of at least a factor of about 2 times the metal cation concentration, in further embodiments, at least a factor of about 3, in other embodiments at least a factor of about 4 and in additional embodiments a factor from about 5 to about 25 times the metal cation concentration.

(EX1001, 12:33-39.)

33. The '564 patent further discloses that the greater stability of the precursor solutions results in a higher-quality resulting coating material, where the contrast between irradiated and non-irradiated regions of the coating material is improved:

The precursor solutions have been formulated to achieve very high levels of stability such that the precursor solutions have appropriate shelf lives for commercial products. Also, it has been discovered that the formulation of the precursor solutions can be designed to achieve desired levels of radiation absorption for a selected radiation based on the selection of the metal cations. ... The control of the precursor solution is based on high concentrations of radiation sensitive ligands to the metal cations, specifically peroxide-based ligands. In particular, if the mole ratio of peroxide groups to the metal cations is at least 2, more stable solutions can be formed. The more stable precursor solutions provide an added advantage of greater contrast between the ultimate irradiated coating material and un-irradiated coating material.

(EX1001, 9:55-10:7.)

34. Therefore, as the '564 patent confirms, a person of ordinary skill in the art would have understood that changing the precursor materials to have a higher

percentage of peroxide ligands results in changes to the coating material that is eventually formed. As one example, the '564 patent notes that the coating material demonstrates improved contrast in some situations:

As described herein, significant improvements in the precursor solutions have been accomplished through the use of significantly higher radiation sensitive ligand concentrations. Even more surprisingly, significantly increasing the radiation sensitive ligand concentration in the precursor solutions results in a coating material that has greater contrast following radiation exposure so that there are surprising added benefits where precursor solution stabilization further accomplishes improved patterning and shorter development times.

(EX1001, 6:26-35.)

35. In addition to differences resulting from different concentrations of precursor materials, a person of ordinary skill in the art would have understood that different coating films can also result because of differences in the way in which the precursor materials are combined. For example, the '564 patent discloses a particular mixing sequence where ZrOCl_2 or HfOCl_2 is combined with H_2O_2 , then there is a five-minute rest, then H_2SO_4 is added, and then the solution is again allowed to rest for five minutes. (EX1001, 21:23-55.) The '564 patent discloses

that “[t]his particular mixing sequence has been found to limit particle growth.”
(EX1001, 21:55-56.)

36. A person of ordinary skill in the art would have understood that the ’564 patent, which teaches that the solution resulting from the above mixing sequence is then diluted with “ultrapure water,”³ discloses that performing the mixing of the three materials in that particular order and limiting the resting time after the mixing steps in turn limits the formation of larger, undesirable particles in the solution. The ’564 patent explains that stability of a precursor material is lost “if a phase separation occurs with the production of large sol particles.”⁴ (EX1001,

³ The ’564 patent further discloses that this mixing sequence is used to form a solution that is then diluted with “ultrapure water” to achieve formations of a solution that have a desired concentration of metal. (EX1001, 21:57-66.) A person of ordinary skill in the art would have understood that the final dilution step using purified water both provides a solution with a desired metal concentration as well as slows down any further reaction between the constituent materials combined in the two mixing steps.

⁴ The nanometer-sized original sol/particle size, described in the scientific literature as “radius of gyration,” is a size-related value collected by techniques such as small-

13:16-17.) In other words, the constituent parts of the precursor material combine and produce large particles that make the precursor less useful in the desired combination for which the precursor is designed.

37. A person of ordinary skill in the art would have understood that, similarly, allowing the mixtures to rest for too long of a time period could allow for unwanted reactions between the precursor materials (e.g., those that produce “large sol particles”) and thereby make the resulting solution less useful for forming the desired coating material. Therefore, a person of ordinary skill in the art would have understood that coating films with different characteristics can also result when there are differences in the way in which the precursor materials are combined, where one such difference may be the resting time after one mixing operation before another mixing operation is commenced.

38. A person of ordinary skill in the art would have known and appreciated that other aspects of the coating film formation process can also influence the characteristics of the resulting coating film. For example, as discussed immediately above, the '564 patent discloses diluting the solution resulting from mixing the

angle X-ray scattering, which contains information about size, shape, symmetry, and homogeneity. Smaller values indicate smaller unit particles which would result in the possibility for thinner and more uniform films.

precursor materials to achieve a desired concentration of metal ions. (EX1001, 21:62-64 (“Using the method described above, a 30 mL formulation of an Hf based precursor solution with a final hafnium concentration of 0.15 M was obtained.”).)

In this context, the '564 patent explains that having a lower concentration of metal ions in the solution results in lower viscosity, which, in turn, allows for the formation of a thinner coating. (EX1001, 5:11-17 (“In some embodiments, the inorganic precursor solution can have a relatively low concentration of metal ions such that the rheology of the coating composition, e.g., the viscosity, allows the formation of a thin coating on the substrate. The use of a thinner coating is consistent with the formation of higher resolution structures upon exposure to radiation and development of the pattern.”), 6:50-54 (“The metal ion concentration can be selected to provide desired properties for the precursor solution, with more dilute solutions generally consistent with the formation of thinner coating materials.”), 13:4-9 (“The concentrations of the species in the precursor solutions can be selected to achieve desired properties of the solution. In particular, lower concentrations overall can result in a desirable properties of the solution for certain coating approaches, such as spin coating, can achieve thinner coatings using reasonable coating parameters.”).) A person of ordinary skill in the art would have understood that a final hafnium concentration in the Hf-based precursor solution greater than the 0.15 M disclosed in the '564 patent could impact the ability to deposit the resulting

coating to the desired thickness as thinner coatings are more difficult to achieve with higher metal concentrations due to increased viscosity.

39. As demonstrated by the examples that I present above, a person of ordinary skill in the art would have understood that the characteristics of the coating formed can be impacted by a number of factors, including concentrations of materials in the precursor solutions, the time allowed for combination of the precursor solutions, and the level of dilution of the solution used to deposit the coating layer by spin coating.

VIII. CHANGES TO MATERIALS BASED ON EXPOSURE TO UV OR EUV RADIATION

40. I have been asked to consider, in the context of films that are exposed to UV or EUV as a part of a patterning process, whether such exposure necessarily results in the altering of chemical properties of the films that results in differential dissolution rates. As I explain below, patterning of such films in processes that include exposure to UV or EUV radiation does not require the exposure to change chemical properties in a manner that results in differential dissolution rates.

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).)

42. Similarly, a person of ordinary skill in the art also would have known that chemical changes that result in different dissolution rates can be driven by aspects of the lithography process besides the actual exposure to light/radiation. For example, post-exposure bake operations, where the substrate is heated after exposure, was known to result in chemical reactions that made portions of the resist susceptible to removal while leaving other portions behind:

As shown in step 30, the wafer may be subjected to a post exposure bake process step. The post exposure bake process may be used to drive a chemical reaction in the exposed portions of the resist such that portions of the resist maybe removed in subsequent processing. As such, the performance of the post exposure bake process may be critical to the performance of the lithography process.

(EX2005, 8:20-26.)

43. Therefore, a person of ordinary skill in the art would have understood that exposure to UV or EUV radiation can result in either physical or chemical changes to the resist material. While such changes can result in differential dissolution rates between exposed and unexposed regions, the differential dissolution rates used for patterning the exposed resist can also be the result of steps

in the lithography process other than the actual exposure to the radiation, such as the post-exposure bake referenced above. (EX2007, 7 (“Upon irradiation, acids photogenerated from a PAG catalytically *cleaves t-BOC groups during postexposure bake (PEB)* at high temperature as shown in FIG. 9”) (emphasis added).) Indeed, a person of ordinary skill in the art would have understood that exposure may result in chemical changes to the exposed portions that, by themselves, do not produce differential dissolution rates. In such a scenario subsequent processing steps are required in order to induce further chemical changes that produce those differential dissolution rates used for patterning the resist.

IX. CHANGE IN EXTINCTION COEFFICIENT OR ABSORPTION COEFFICIENT DOES NOT MEAN A MATERIAL IS A RADIATION SENSITIVE LIGAND

44. For claim 1’s limitation requiring that the “coating material comprises ... radiation sensitive ligands,” I understand that Dr. Holland relies on a theory based on disclosures regarding an “extinction coefficient” in Stowers 2008. Stowers 2008 states “[i]t is expected that these extinction coefficients will be different with the presence of peroxide in the as-deposited material.” (EX1008, 69.) Dr. Holland explains that an “extinction coefficient is a property that determines how strongly a material absorbs radiation at a particular wavelength.” (EX1002, ¶100.)

45. It does not logically, or scientifically, follow that if a mixture (e.g., HafSO_x plus peroxide) is “expected” to have a different extinction coefficient than

the original material (e.g., HafSO_x), 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.

46. For this reason, a person of ordinary skill would not have understood Stowers 2008’s disclosure that it “expected” the extinction coefficient to change to indicate Stowers 2008’s films included a “radiation sensitive ligand,” as required by claim 1 of the ’564 patent.

47. I understand Dr. Holland relies on the same faulty theory for Trikeriotis. Dr. Holland points to a statement in Trikeriotis that “[t]he absorption coefficient of the film depends on the ligand and the synthesis method that was used.” (EX1002, ¶ 152.) I note that Dr. Holland cuts off the second half of the sentence regarding “the synthesis method that was used.” (EX1024, 18.) For the reasons described above, the fact that a particular material (here, ligands disclosed in Trikeriotis) might affect the absorption coefficient because they constitute a part of the total material being analyzed does not necessarily make them “radiation sensitive.”

X. MASS DENSITY OF A MATERIAL IS NOT THE ONLY FACTOR IN DETERMINING A RESIST FILM'S EUV ABSORPTION

48. For claim 7, Dr. Holland proposes a theory that EUV absorbance for Stowers 2008 films is higher than conventional resists because the density of HafSO_x and ZircSO_x materials is higher than materials in conventional resists, such as PMMA. (EX1002, ¶¶136-139.)

49. Dr. Holland's theory is based on a "linear trend" proposed between "calculated linear absorption coefficient" and "calculated density" in a journal article directed to conventional polymer resists (i.e., not inorganic resists like HafSO_x and ZircSO_x). (EX1025, 4.) But this is merely a trend, it is not necessarily the case that higher density necessarily means higher EUV absorption.

50. A simple example, based on Dr. Holland's own evidence, shows why it is not necessarily the case that a higher mass density of a material equates to higher calculated linear absorption coefficient. Dr. Holland relies on Figure 3 of EX1025, pointing to the data point for PMMA. (EX1002, ¶ 136.) According to Dr. Holland's theory, data points having a higher mass density will necessarily have a higher calculated linear absorption coefficient. But that is not true. Several data points in this figure have higher density and *lower* calculated linear absorption coefficient than PMMA, for example:

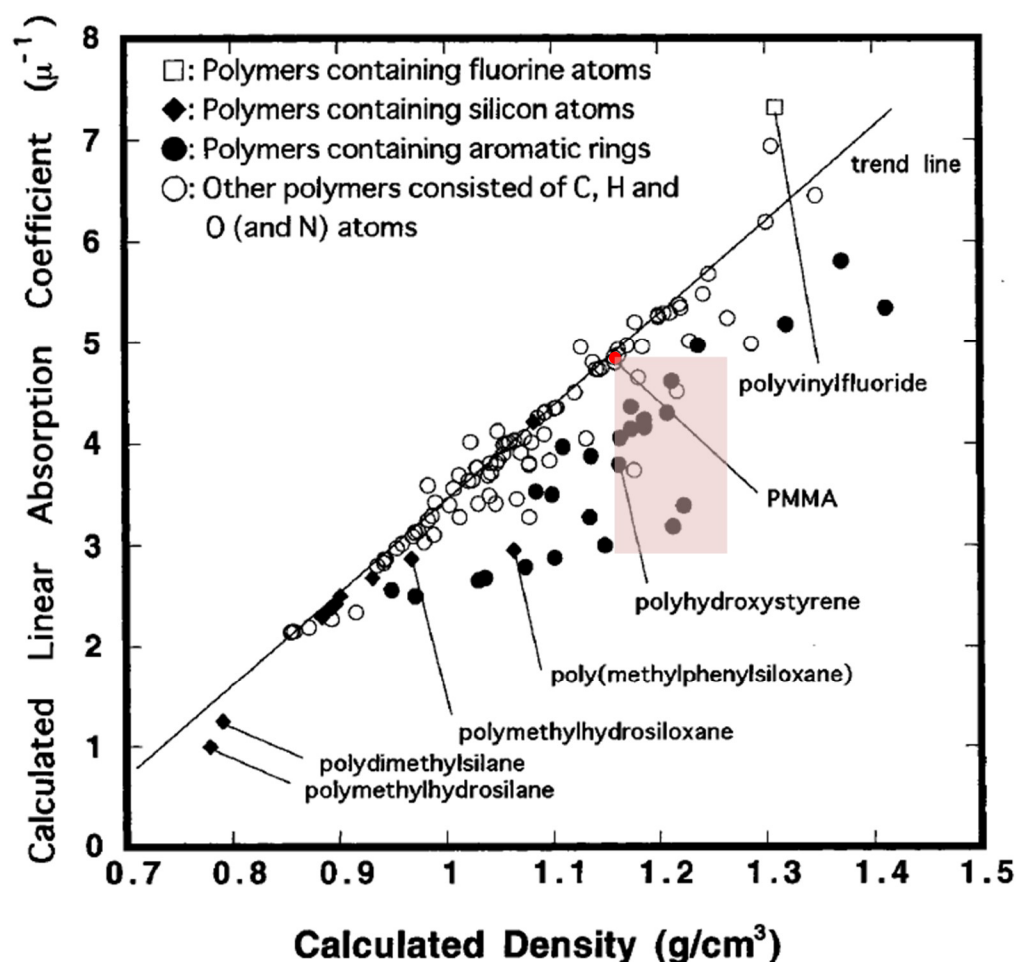


Figure 3. Calculated linear absorption coefficient versus calculated density.

(EX1025, 4 (red annotation added to show PMMA datapoint, and pink annotation added to show data points with higher density and lower calculated linear absorption coefficient).)

51. I understand Dr. Holland relies on the same faulty theory for Trikeriotis. Dr. Holland points to a statement in EX1026—which seems to be discussing hafnium oxide films for dielectric applications, not photoresists—that “[f]or thicker films, densities close to the expected bulk density of 9.68 g cm^{-3} have been

measured.” (EX1002, ¶158 (citing EX1026, 4).) Dr. Holland argues this shows a “POSA would have known that the density of hafnium oxide is approximately 9.68 g/cm³.” (EX1002, ¶ 158.) Dr. Holland argues that this mass density is higher than the “approximate density” of PMMA at 1.19 g/cm³. (EX1002, ¶ 158.) But even assuming those numbers were correct for the mass density of those materials, for the reasons described above, the fact that a particular material has a higher mass density does not necessarily equate to higher EUV absorbance in a film.

XI. DR. HOLLAND’S ALLEGED CORRELATION BETWEEN ELECTRON BEAM DOSE AND EUV DOSE

52. For claim 12, Dr. Holland relies on patterning of “ZircSO_x films” with electron beam in Chapter 4 of Stowers 2008. (EX1002, ¶145 (citing EX1008, 89).) Specifically, Dr. Holland points to a teaching that “16 nm wide isolated features can be patterned at a dose of 112 μC/cm².” (EX1008, 89.) This dose is in units appropriate for electron beam patterning, not EUV, as the claim requires.

53. Dr. Holland attempts to correlate this electron beam dose in Stowers 2008 with an EUV dose. Dr. Holland points to an article dated 2011 (which I understand to be after the priority date of the ’564 patent) stating a particular correlation between an electron beam dose and an EUV dose for a HafSO_x film. (EX1022, 7.) But Dr. Holland has not provided any reasoning or basis for applying

a dose correlation for a HafSO_x film to a ZircSO_x film. And I am not aware of any such basis.

54. After reading the EX1022 article, it is clearly directed to HafSO_x. For instance, in the paragraph describing the dosing correlation on which Dr. Holland relies, EX1022 is describing “Improved Materials” and “New resist compositions and synthesis approaches [that] have resulted in an improved formulation.” (EX1022, 7.) As explained earlier in the article, “[f]or the current generation of Inpria’s EUV resists, *we have selected hafnium* as the metal because of its high EUV absorption cross section relative to many other metals.” (EX1022, 3 (emphasis added).) Although the article also refers to the more general terms “metal oxide precursors” and “MSO_x”—which stands for “metal oxide sulfate”—the article repeatedly refers to “hafnium,” never mentioning zirconium or ZircSO_x. (EX1022, 3, 9 (“Since the resist is wholly inorganic, with hafnium as a major constituent ...”), 10 (referring to “the relatively high concentration of hafnium”), 11 (“MSO_x materials are chemically similar to inert hafnia”).) Based on this a person of ordinary skill would have understood this article to be disclosing a correlation for a HafSO_x film.

XII. DR. HOLLAND'S EVIDENCE INDICATES TRIKERIOTIS'S ORGANIC LIGANDS ARE NOT THE RADIATION SENSITIVE MATERIAL IN ITS FILMS

55. For the limitation in claim 1 reciting “coating material comprises metal ions with radiation sensitive ligands,” (EX1001, 24:8-10,) Dr. Holland points to “[h]afnium oxide nanoparticles” and “organic ligands” described in Trikeriotis. (EX1002, ¶152.) The only explanation Dr. Holland gives for her belief that the “organic ligands” meet the claim limitation is a statement in Trikeriotis that the “absorption coefficient of the films depends on the ligand.” (EX1024, 18.) This theory is faulty for the reasons I explained above in Section IX.

56. Furthermore, I understand that Dr. Holland relies on a different article (EX1027, “Ober”) written by Christopher Ober and Emmanuel Giannelis (who are also named authors on Trikeriotis, (EX1024, 15)). Dr. Holland suggests this article further describes “the films of the Trikeriotis reference.” (EX1002, ¶161 n.6.) The Ober article, however undermines Dr. Holland’s description of how Trikeriotis allegedly discloses “metal ions with radiation sensitive ligands.”

57. Similar to Trikeriotis, Ober describes a metal oxide core (e.g., HfO_2) surrounded by organic ligands. (EX1027, 1 (describing a “hafnium oxide (HfO_2) core with a diameter of 2nm, surrounded by organic ligands (binding molecules)”)). Ober includes an illustration of the nanoparticle with organic ligands in Figure 1:

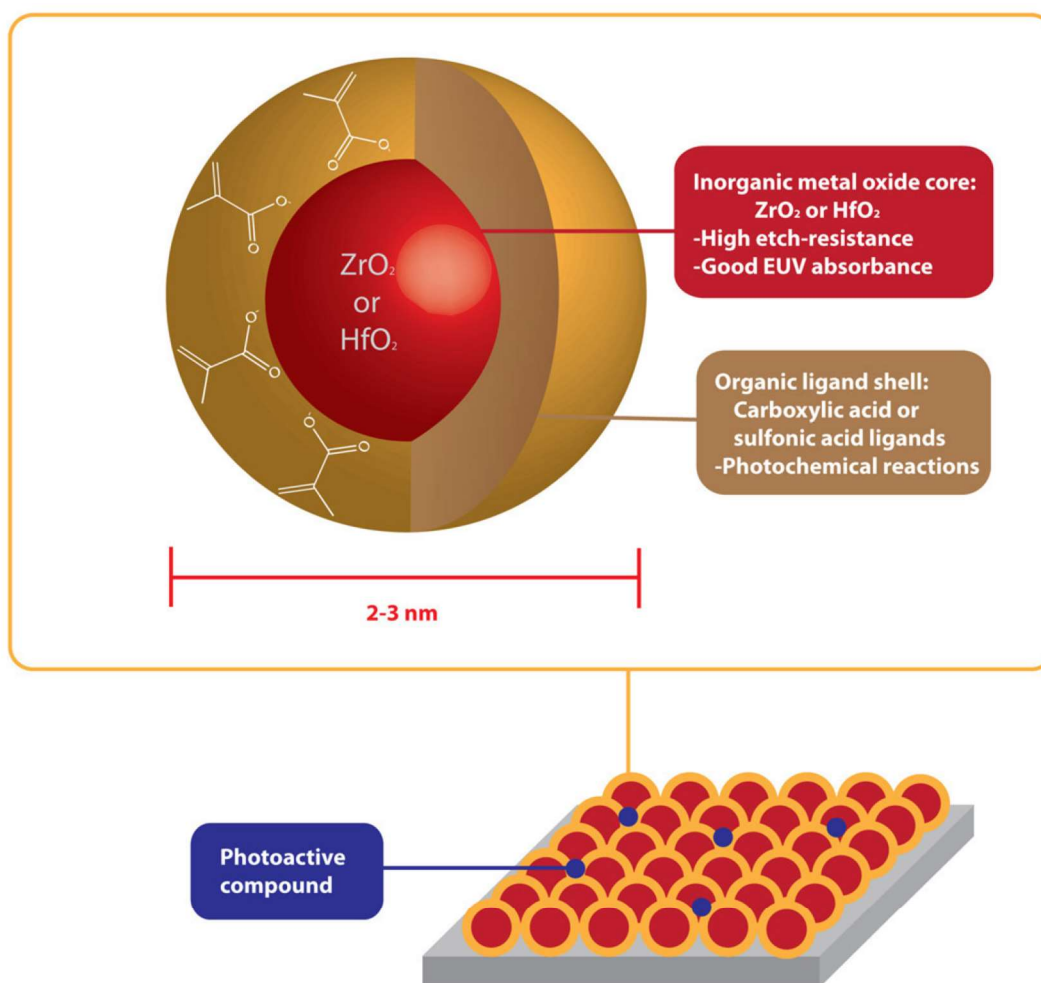


Figure 1. Schematic of the extreme-UV (EUV) nanoparticle photoresist with its core metal oxide and the organic ligand surrounding the core. ZrO_2 : Zirconium dioxide. HfO_2 : Hafnium oxide.

58. As can be seen above, Ober displays the “organic ligand shell” as being a coating attached to the zirconium or hafnium oxide core.⁵ Beneath the blown-up

⁵ Although Figure 1 describes the “Organic ligand shell” as “Carboxylic acid or sulfonic acid ligand” and says the words “Photochemical reactions,” I understand

illustration of the nanoparticle in Figure 1 is the film, which shows “photoactive compound” in blue. Ober describes that it is the “photoactive compound” that is the radiation sensitive part of the film, not the “organic ligands” that Dr. Holland pointed to in her declaration. This is illustrated in Figure 2 of Ober:

this to be describing photochemical reactions that occur due to the photoactive compound in the film, not reactions in the organic ligands themselves (e.g., the methacrylate ligand displayed within the gold color). This is explained further in Ober, where he discusses the photoacid generator that produces sulfonic acid that displaces the methacrylate ligands. (EX1027, 2 (also describing “2-2-dimethoxy-2-phenylacetophenone” as a “photoradical generator” which produces benzoate and acts “[s]imilarly.”).)

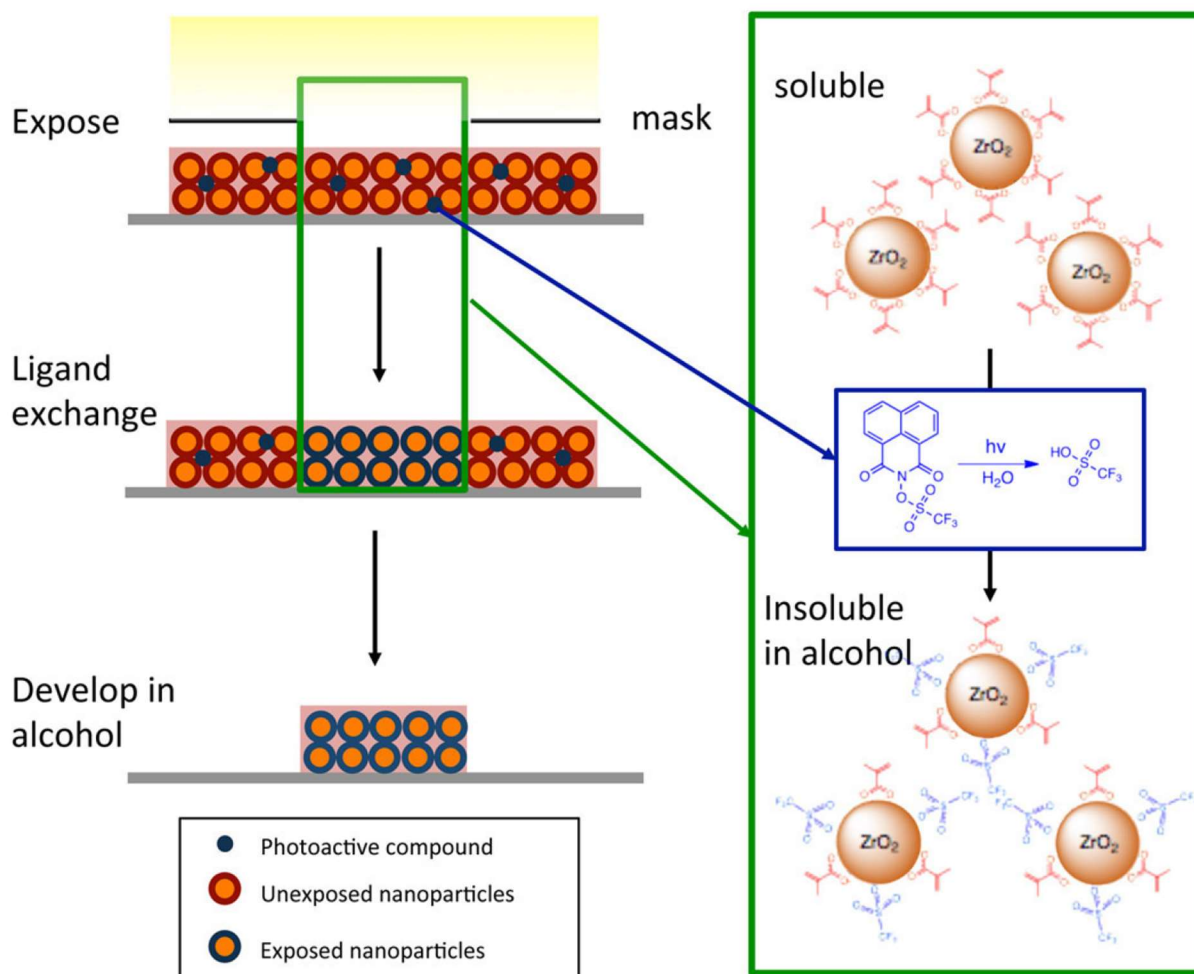


Figure 2. Schematic of the ligand-displacement patterning mechanism for negative-tone pattern formation. $h\nu$: Energy. H_2O : Water.

(EX1027, 2 (Fig. 2).)

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” that are reacting to the radiation (“ $h\nu$: Energy”) and which act on the nanoparticles

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.

XIII. CONCLUSION

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

Dated: July 31, 2024

By: 

Sanjay Banerjee, Ph.D.