

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

Taiwan Semiconductor Manufacturing Company Limited

Petitioner

v.

Godo Kaisha IP Bridge 1

Patent Owner

**DECLARATION OF DR. SANJAY K. BANERJEE
IN SUPPORT OF PETITION FOR *INTER PARTES* REVIEW OF UNITED
STATES PATENT NO. 6,538,324**

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I, Sanjay Kumar Banerjee, declare as follows:

I. INTRODUCTION

1. My name is Dr. Sanjay Kumar Banerjee. I have been asked to submit this declaration on behalf of Taiwan Semiconductor Manufacturing Company Limited (“TSMC” or “Petitioner”) for a petition for *inter partes* review of U.S. Patent No. 6,538,324 (“the ’324 patent”), which I understand is being submitted to the Patent Trial and Appeal Board of the United States Patent and Trademark Office by TSMC. I have been told that the ’324 patent is owned by Godo Kaisha IP Bridge 1.

2. I have been retained as a technical expert by TSMC to study and provide my opinions on the technology claimed in, and the patentability or non-patentability of, claims 1-3, 5-7, and 9 in the ’324 patent (“Challenged Claims”). I have also been asked to provide my opinions regarding the level of ordinary skill in the art at the time the Japanese priority application of the U.S. application leading to the ’324 patent was filed, which I have been told was June 24, 1999.

II. SUMMARY OF OPINIONS

3. Based on my experience, knowledge of the art at the relevant time, analysis of prior art references, and the understanding a person of ordinary skill in the art would give to the claim terms in light of the specification, it is my opinion

that all of the Challenged Claims of the '324 patent are unpatentable as being obvious over the prior art references I discuss below.

III. BACKGROUND AND QUALIFICATIONS

A. Background

4. 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.

5. I have also been active in industries related to the relevant field of semiconductor processing for integrated circuits. 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 DRAM, for which I was co-recipient of the Best Paper Award, IEEE International Solid State Circuits Conference, 1986.

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

7. I am a leading researcher and educator in various areas of transistor 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.

8. At the University of Texas, I am the director of the Microelectronics Research Center, comprised of faculty colleagues, graduate, and undergraduate students. I also serve 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 1,000 technical articles; many related to semiconductor fabrication technology, most at highly competitive refereed conferences and rigorously reviewed journals. I have also published 8 books or chapters on transistor device physics and fabrication, and have supervised over 50 Ph.D. and 60 MS students.

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 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 in 1988, and several SRC Inventor Recognition and 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).

15. I am the inventor or co-inventor of over 30 United States patents in various areas of transistor device fabrication technology.

16. Additional details about my employment history, fields of expertise, and publications are further included in my curriculum vitae (attached as Appendix A).

B. Previous Expert Witness Experience

17. I have served as an expert witness since the mid 1990's. In the last ten years or so, I have testified at the ITC three times, and the Northern District of California once. In addition, I have been deposed six times on patents related to CMOS and semiconductor memories such as flash and DRAMs. Several of these have been in IPR cases.

C. Compensation

18. I am being compensated for services provided in this matter at my usual and customary rate of \$500 per hour plus travel expenses. My compensation

is not conditioned on the conclusions I reach as a result of my analysis or on the outcome of this matter. Similarly, my compensation is not dependent upon and in no way affects the substance of my statements in this declaration.

19. I have no financial interest in Petitioner or any of its subsidiaries. I also do not have any financial interest in Godo Kaisha IP Bridge 1. I do not have any financial interest in the '324 patent and have not had any contact with any of the named inventors of the '324 patent (Masayoshi Tagami and Yoshihiro Hayashi).

IV. MATERIALS REVIEWED

20. In forming my opinions, I have reviewed the following materials:

Exhibit 1001:	U.S. Patent No. 6,538,324 to Tagami et al.
Exhibit 1002:	File History of U.S. Patent No. 6,538,324 to Tagami et al.
Exhibit 1004:	U.S. Patent No. 5,893,752 to Zhang et al.
Exhibit 1005:	U.S. Patent No. 6,887,353 to Ding et al.
Exhibit 1006:	Holloway et al., "Tantalum as a diffusion barrier between copper and silicon: Failure mechanism and effect of nitrogen additions," Journal of Applied Physics, 71(11), 5433-5444 (1992).
Exhibit 1007:	Sun et al., "Properties of reactively sputter-deposited Ta-N thin films," Thin Solid Films, 236 (1993) 347-351.
Exhibit 1008:	U.S. Patent No. 5,858,873 to Vitkavage et al.
Exhibit 1009:	U.S. Patent No. 5,668,411 to Hong et al.

- Exhibit 1010: Excerpt of El-Kareh, "Fundamentals of Semiconductor Processing Technologies," Kluwer Academic Publishers (1995).
- Exhibit 1015: Stavrev et al., "Crystallographic and morphological characterization of reactively sputtered Ta, Ta-N and Ta-N-O thin films," Thin Solid Films, 307 (1997) 79-88.
- Exhibit 1017: Duan et al., "Magnetic Property and Microstructure Dependence of CoCrTa/Cr Media on Substrate Temperature and Bias," IEEE Transactions on Magnetics, Vol. 28, No. 5, September 1992.
- Exhibit 1019: Moussavi et al., "Comparison of Barrier Materials and Deposition Processes for Copper Integration," Proceedings of the IEEE 1998 International Interconnect Technology Conference, pp. 295-97 (1998).
- Exhibit 1021: Wijekoon et al., "Development of a Production Worthy Copper CMP Process," 1998 IEEE/SEMI Advanced Semiconductor Manufacturing Conference, pp. 354-63 (1998).
- Exhibit 1023: Wang et al., "Barrier Properties of Very Thin Ta and TaN layers Against Copper Diffusion," J. Electrochem. Soc., Vol. 145, No. 7, pp. 2538-45.

V. LEGAL STANDARDS

21. I am not an attorney and have not been asked to offer my opinion on the law. However, as an expert offering an opinion on whether the claims in the '324 patent are patentable, I understand that I am obliged to follow existing law. I have been told the following legal principles apply to analysis of patentability

pursuant to 35 U.S.C. §§ 102 and 103 as those statutes existed prior to the changes of the America Invents Act.¹

22. I also have been told that, in an *inter partes* review proceeding, patent claims may be deemed unpatentable if it is shown by preponderance of the evidence that they were anticipated and/or rendered obvious by one or more prior art patents or publications.

A. Anticipation

23. I have been told that for a claim to be anticipated under pre-AIA 35 U.S.C. § 102, every limitation of the claimed invention must be found in a single prior art reference. I have been asked to assume each of Exhibits 1004-1010, 1015, 1017, 1019, 1021, and 1023 qualifies as prior art to the Challenged Claims of the '324 patent.

24. I have been told that a claim is unpatentable as anticipated under pre-AIA § 102(a) if the claimed invention was “known or used by others in this country, or patented or described in a printed publication in this or another country, before the invention thereof by the applicant for patent.”

¹ I was told Congress changed U.S. patent law in the American Invents Act, Pub. L. No. 112-29, 125 Stat. 284 (2011) (“AIA”). I was also told that the '324 patent is governed by statutes as they existed prior to the enactment of the AIA.

25. I understand that a claim is unpatentable as anticipated under pre-AIA § 102(b) if the claimed invention was “patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States.”

26. I also understand that a claim is unpatentable as anticipated under pre-AIA § 102(e) if “the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for the purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.”

B. Obviousness

27. I have been told that under pre-AIA 35 U.S.C. § 103(a), “[a] patent may not be obtained although the invention is not identically disclosed or described as set forth in section 102, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole

would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.”

28. When considering the issues of obviousness under pre-AIA § 103, I have been told that I am to do the following:

- a. Determine the scope and content of the prior art;
- b. Ascertain the differences between the prior art and the claims at issue;
- c. Resolve the level of ordinary skill in the pertinent art; and
- d. Consider evidence of secondary indicia of non-obviousness (if available).

29. I have been told that the relevant time for considering whether a claim would have been obvious to a person of ordinary skill in the art under pre-AIA § 103 is the time of alleged invention.

30. I have been told that obviousness is a determination of law based on underlying determinations of fact. I have been told that these factual determinations include the scope and content of the prior art, the level of ordinary skill in the art, the differences between the claimed invention and the prior art, and secondary considerations of non-obviousness.

31. With respect to secondary indicia of non-obviousness, I have been told that such evidence may include the following:

- a. Commercial success: I have been told that a strong showing of commercial success that can be attributed to the merits of the invention should be considered an indication of non-obviousness.
- b. Copying: I have been told that evidence that if others have copied the patented invention, as opposed to a prior art device, which is an indication of non-obviousness.
- c. Long-standing problem or need: I have been told that evidence of a persistent problem or need in the art that was resolved by the patented invention is an indication of non-obviousness.
- d. Prior failure: I have been told that evidence that others have tried and failed to solve the problem is an indication of non-obviousness.
- e. Commercial acquiescence of competitors: I have been told that the willingness of industry to license the patent at issue is an indication of non-obviousness, though consideration must be given to distinguishing respect for the invention from a desire to avoid litigation.
- f. Skepticism: I have been told that evidence that those of ordinary skill were skeptical as to the merits of the invention, or even taught away from the invention, are indications of non-obviousness.
- g. Independent development: I have been told that evidence that others developed the claimed invention about the same time is an indication of obviousness. In contrast, I also have been told that failure to do so is an indication of non-obviousness.
- i. Unexpected results: I have been told that evidence that those of ordinary skill in the art were surprised by the capabilities of the claimed invention is an indication of non-obviousness.

32. I have been told that any assertion of the above secondary indicia must be accompanied by a nexus between the merits of the invention and the evidence offered.

33. I have been told that a reference may be combined with other references to disclose each element of the invention under pre-AIA § 103. I have been told that a reference may also be combined with the knowledge of a person of ordinary skill in the art and that this knowledge may be used to combine multiple references. I have also been told that a person of ordinary skill in the art is presumed to know the relevant prior art. I have been told that the obviousness analysis may take into account the inferences and creative steps that a person of ordinary skill in the art would employ.

34. In determining whether a prior art reference could have been combined with another prior art reference or other information known to a person having ordinary skill in the art, I have been told that the following principles may be considered:

- a. A combination of familiar elements according to known methods is likely to be obvious if it yields predictable results;
- b. The substitution of one known element for another is likely to be obvious if it yields predictable results;
- c. The use of a known technique to improve similar items or methods in the same way is likely to be obvious if it yields predictable results;
- d. The application of a known technique to a prior art reference that is ready for improvement, to yield predictable results;

- e. Any need or problem known in the field and addressed by the reference can provide a reason for combining the elements in the manner claimed;
- f. A person of ordinary skill often will be able to fit the teachings of multiple references together like a puzzle; and
- g. The proper analysis of obviousness requires a determination of whether a person of ordinary skill in the art would have a “reasonable expectation of success”—not “absolute predictability” of success—in achieving the claimed invention by combining prior art references.

35. I have been told that whether a prior art reference renders a patent claim unpatentable as obvious is determined from the perspective of a person of ordinary skill in the art. I have been told that, while there is no requirement that the prior art contain an express suggestion to combine known elements to achieve the claimed invention, a suggestion to combine known elements to achieve the claimed invention may come from the prior art as a whole or individually, as filtered through the knowledge of one skilled in the art. In addition, I have been told that the inferences and creative steps a person of ordinary skill in the art would employ are also relevant to the determination of obviousness.

36. I have been told that, when a work is available in one field, design alternatives and other market forces can prompt variations of it, either in the same

field or in another. I have been told that if a person of ordinary skill in the art can implement a predictable variation and would see the benefit of doing so, that variation is likely to be obvious. I have been told that, in many fields, there may be little discussion of obvious combinations, and in these fields market demand—not scientific literature—may drive design trends. I have been told that, when there is a design need or market pressure and there are a finite number of predictable solutions, a person of ordinary skill in the art has good reason to pursue those known options.

37. I have been told that there is no rigid rule that a reference or combination of references must contain a “teaching, suggestion, or motivation” to combine references. But I also have been told that the “teaching, suggestion, or motivation” test can be a useful guide in establishing a rationale for combining elements of the prior art. I have been told that this test poses the question as to whether there is an express or implied teaching, suggestion, or motivation to combine prior art elements in a way that realizes the claimed invention, and that it seeks to counter impermissible hindsight analysis.

VI. TECHNOLOGICAL BACKGROUND

38. U.S. Patent No. 6,538,324 (Ex. 1001) addresses problems relating to diffusion barriers for use with copper interconnects that were heavily investigated in the 1990s because their solutions were necessary to scale semiconductor devices

to smaller sizes. *See, e.g.*, Ex. 1001, 1:13-19. As I discuss below, the '324 patent's solution had been taught in prior art. In my opinion, it was at best merely an obvious combination of existing technology used to solve the same problem.

39. As background, semiconductor devices, such as transistors, are typically formed using layers of material deposited on a semiconductor substrate, such as silicon. Once formed, the semiconductor devices include electrical terminals that are interconnected by one or more metal wiring layers to form specific circuitry, for example, in a processor. A metal wiring layer is often deposited over an interlayer insulating layer, such as silicon dioxide, which separates the metal wiring layer from underlying layers of the semiconductor devices (such as MOSFETs).

40. To my knowledge, at the time the '324 patent was filed, those of ordinary skill in the art knew that copper was a desirable metal for the wiring layer as devices became smaller in size, since copper provided lower electrical resistivity relative to aluminum. As MOSFETs got smaller and faster, the interconnect delays became more and more important as a fraction of the overall delay; thus copper started supplanting the older aluminum based interconnect technology in silicon microelectronics. Ex. 1001, 1:13-19. But it was also known that "it is absolutely necessary for a semiconductor device having a copper wiring layer to have a diffusion-barrier film for preventing diffusion of copper into an interlayer

insulating film formed between copper wiring layers.” *Id.*, 1:26-30. It is also important to prevent diffusion of copper into the silicon substrate where it can create electrical defects which degrade MOSFET performance. Diffusion occurs when atoms or molecules migrate from an area of higher concentration into an area of lower concentration. Thus, I understand that the problem in the ’324 patent concerned blocking the movement of copper from a wiring layer having a high concentration of copper into an underlying insulating layer and semiconductor devices. *See id.*, 1:22-25 (explaining that copper has a high diffusion rate in silicon and silicon dioxide, and if copper were to diffuse into a MOSFET formed on a silicon substrate, it would induce a reduction in carrier lifetime in such a device, and thus increase leakage current in MOSFETs and other devices).

41. The ’324 patent specification further explains it was known that the diffusion barrier not only must prevent copper from diffusing out of the wiring layer into underlying layers and devices, but also must provide good adhesion to the copper wiring layer. *Id.*, 2:13-15 (“As will be obvious to those skilled in the art, the diffusion-barrier film is required to have high coverage as well as capability of preventing copper diffusion and adhesion to copper.”); *see also id.*, 1:30-33. The specification acknowledges that several known copper-diffusion barrier films existed at the time of the alleged invention. *Id.*, 2:21-54, 7:52-57, FIGS. 1-3.

42. The purported invention is a two-layer diffusion barrier to prevent copper diffusion and provide good adhesion to a copper wiring layer and the interlayer insulating film.² The bottom layer in the diffusion barrier is an amorphous metal nitride to prevent copper diffusion. *See, e.g., id.*, Abstract, 9:50-52, 18:22-24. The top layer is a crystalline metal that contains nitrogen to provide good adhesion to a copper wiring layer. *See, e.g., id.*, Abstract, 9:49-50, 18:24-26. The claims require the crystalline layer of the diffusion barrier to contain less nitrogen than the amorphous layer. *Id.*, 19:2-3.

43. In my opinion, the two-layer diffusion barrier, combining known crystalline and amorphous barrier layers, disclosed and claimed in the '324 patent was not new and non-obvious. As shown, for example, in FIG. 1 of the patent, two-layer diffusion barriers for preventing copper diffusion were already known in the art. *Id.*, 7:51-52. It was also known that a crystalline film could provide good adhesion to a copper wiring layer, although it exhibited a “low barrier characteristic of preventing copper diffusion.” *Id.*, 3:1-4, 3:14-19. And it was

² The '324 patent's specification and claims refer to a barrier “film” (i.e., thin film) having a multi-layered structure of first and second films. In this context, the words “layer” and “film” are used interchangeably.

known that amorphous (non-crystalline) films provide a better barrier to copper diffusion, though they do not adhere as well to copper. *Id.*, 3:21-33.

44. In my opinion, others in the field had already put these pieces together to devise two-layer diffusion barriers with a crystalline layer for its known characteristics of providing good adhesion to copper, and an amorphous layer for its known property of preventing copper diffusion into underlying semiconductor devices, e.g., incorporating the prior-art films in FIGS. 2 and 3 into the barrier structure in FIG. 1. And more particularly, others had already made two-layer diffusion barriers using a crystalline layer for providing good adhesion to copper and an amorphous layer for preventing copper diffusion. They had also described such two-layer diffusion barriers in which the amorphous layer was tantalum nitride (TaN_x) and the crystalline layer was a tantalum (Ta) metal containing nitrogen. For example:

- U.S. Patent No. 5,893,752 (“*Zhang*”, Ex. 1004) discloses a two-layer diffusion barrier having a bottom TaN_x layer for preventing copper diffusion and a top “tantalum-rich nitride film [that] is substantially pure tantalum” for providing good adherence to a copper wiring layer.

Ex. 1004, Abstract, 2:29-40, 3:22-67, FIG. 8 (multi-layer diffusion barrier 22 and 32, copper wiring layer 54 and 64)³, FIG. 4.

- U.S. Patent No. 6,887,353 (“*Ding*”, Ex. 1005), directed to the same problem as the ’324 patent and *Zhang*, teaches that the TaN_x layer in *Zhang* would be an amorphous layer and the adjacent layer of tantalum-rich nitride film would be crystalline. Ex. 1005, Abstract, 3:33-38, 7:66-8:4.
- Other prior art also discuss properties of Ta-based diffusion barriers at different nitrogen contents for preventing copper diffusion. For example, Sun et al., “Properties of reactively sputter-deposited Ta-N thin films,” Thin Solid Films, vol. 236, nos. 1-2, pages 347-351 (1993) (“*Sun*”, Ex. 1007) discloses that “In substantial atomic concentrations, nitrogen can also promote the formation of amorphous metallic alloys with most early transition metals,” such as Ta, and the resulting amorphous films exhibit an “absence of fast diffusion paths” as compared with polycrystalline films. Ex. 1007 at 9.

³ *Zhang* teaches the copper seed film 54 and copper wiring film 64 may be replaced with a single copper film. Ex. 1004, 5:35-38.

A. Diffusion Barrier Basics

45. To my knowledge, copper had been widely used as interconnect material in semiconductor devices due to its improved properties over aluminum, such as smaller resistivity. *See, e.g.*, Ex. 1005, 1:15-23 (“[c]opper offers a significant improvement over aluminum as a contact and interconnect material. For example, the resistivity of copper is about $1.67\ \mu\Omega\text{cm}$, which is only about half of the resistivity of aluminum”). However, it had been recognized that “copper diffuses rapidly into adjacent layers of SiO_2 and silicon and needs to be encapsulated.” *Id.*, 1:60-62. To prevent copper diffusion, “[a]ttempts have been made to use tantalum and tantalum related compounds . . . as a barrier/adhesion film for a copper interconnect.” Ex. 1004, 1:27-31. To my knowledge, various tantalum-based materials had been studied for using in copper diffusion barriers. *See, e.g.*, Ex. 1006; Ex. 1007.

46. A tantalum-based barrier can have no nitrogen (Ta), have more tantalum than nitrogen (nitrogen-alloyed Ta or tantalum-rich tantalum nitride), have about the same amount of tantalum and nitrogen (stoichiometric composition TaN), or have more nitrogen than tantalum. For example, *Zhang* discloses a tantalum nitride “close to the stoichiometric composition (TaN)” for using in diffusion barriers. Ex. 1004, 3:39-41. Stoichiometric composition describes the amounts of substances that are involved in reactions to form a compound, which is

usually a thermodynamically stable compound. For tantalum nitride, the stoichiometric composition is TaN, with a Ta-to-N stoichiometric ratio of 1:1, which can also be referred to as tantalum mononitride. Under some deposition conditions such as sputtering at low substrate temperatures, it is possible to form sub-stoichiometric TaN_x materials, where x is less than 1.

47. I believe that a person of ordinary skill in the art (“POSITA”) as of the filing date of the ’324 patent would have recognized that tantalum-based materials may have certain problems when used as copper diffusion barriers. For example, tantalum nitride, although a good diffusion barrier (*see, e.g.*, Ex. 1005, 3:27-29, “tantalum nitride (TaN_x) is a better barrier layer for copper than tantalum (Ta)”), may exhibit other issues such as poor adhesion or wetting with the adjacent copper layer, or not providing the copper layer with desired electromigration characteristics. *See, e.g.*, Ex. 1004, 1:33-34 (“tantalum nitride has adhesion problems with some types of copper films”); Ex. 1005, 8:5-7 (“a higher temperature is required to dewet/delaminate a depositing copper layer from a Ta surface than from a TaN_x surface,” i.e., copper layer is easier to dewet/delaminate from the TaN_x surface), 3:29-32 (“copper deposited directly over TaN_x does not exhibit a sufficiently high degree of <111> crystal orientation to provide the desired copper electromigration characteristics”).

48. “Adhesion” is used to describe the strength of the bonding between two layers. “Wetting” is the ability of a depositing material to form an interface with a surface onto which the material is deposited, and is therefore also a term indicative of strength of the adhesion between layers. A POSITA, as of the filing date of the ’324 patent, would have known that better wetting between the two layers generally leads to better adhesion.

49. As explained in *Ding*, a POSITA would have understood that electromigration refers to “motion of the atoms [in a] thin film conductor” induced by “the application of direct current over particular current density ranges.” This “is said to induce crack or void formation in the conductor which, over a period of time, can result in conductor failure,” which can “severely limit[s] the reliability of the circuit.” *Id.*, 2:10-20.

50. A POSITA would also have recognized that a material can be in different states, such as a crystalline state or an amorphous state. A crystalline state includes a single crystalline state, in which atoms of the material are stacked in a periodic pattern throughout the material; and a polycrystalline state, in which the material contains many small crystals (also referred to as “grains,” separated by grain boundaries along which atoms can diffuse quickly). See, e.g., Ex. 1010, 8. On the other hand, an amorphous material is noncrystalline and lacks long-range or

short-range order, i.e., the atoms are not arranged in a periodic arrangement. *See, e.g., id.*, 9.

51. A crystalline material can be described in terms of a periodic lattice with certain crystalline orientations. *See, e.g., id.*, 9-10. Different crystalline materials may have different arrangements of atoms and different orientation directions, which can be indicated by an index system referred to as Miller indices. *See, e.g., id.*, 11. In this index system, indices in angle brackets, such as $\langle 002 \rangle$ and $\langle 111 \rangle$ mentioned in *Ding* (Ex. 1005, 8:1-4), represent a set of equivalent directions in the crystalline material. Ex. 1010, 11-12. In contrast, an amorphous material does not exhibit any crystalline orientations since the atoms in the amorphous material are randomly arranged.

VII. THE '324 PATENT

A. Claims of the '324 Patent

52. I understand that the patent contains 10 claims. Claim 1 and its dependent claims 2-4 recite a barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate. I also understand that Claim 5 and its dependent claims 6-10 recite a multi-layered wiring structure comprising the barrier film in claim 1.

53. For simplicity, I will refer to elements of the claims using separate reference numbers for each claim element. For example, I will refer to the elements of claim 1, which is representative of the independent claims, as follows:

[1.0] A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films:

[1.1] said first film being composed of crystalline metal containing nitrogen therein,

[1.2] said second film being composed of amorphous metal nitride,

[1.3] said barrier film being constituted of common metal atomic species,

[1.4] said first film being formed on said second film,

[1.5] said first film in direct contact with said second film,

[1.6] said first film containing nitrogen in a smaller content than that of said second film.

54. I will refer to the claim elements of claim 5 as follows:

[5.0] A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate,

[5.1] said barrier film having a multi-layered structure of first and second films,

[5.2] said first film being composed of crystalline metal containing nitrogen therein,

[5.3] said second film being composed of amorphous metal nitride,

[5.4] said barrier film being constituted of common metal atomic species,

[5.5] said first film being formed on said second film,

[5.6] said first film in direct contact with said second film,

[5.7] said first film containing nitrogen in a smaller content than that of said second film.

55. I note that Claim elements [5.2]-[5.7] are identical to elements [1.1]-[1.6] of claim 1.

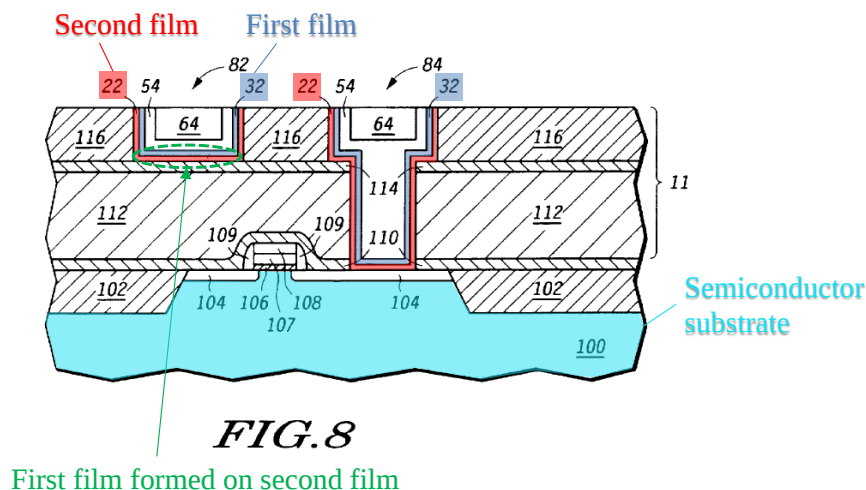
56. I understand from the prosecution history of the '324 patent that the PTO explained that a device covered by claim 1 "could be made by processes materially different from those" of the specific processing steps described in the specification. Ex. 1002 ('324 patent file history) at 202. I agree. The claims recite basic structural compositions that do not reflect their method of manufacture.

B. Prosecution History

57. I understand that the original application for the '324 patent included claims 1-36. Claims 1-10 were directed to either a diffusion barrier film or a structure comprising the diffusion barrier film, and claims 11-36 were directed to methods of forming either the diffusion barrier film or a structure comprising the

diffusion barrier film. I also understand that the Applicant chose to pursue only claims 1-10, and withdrew all of the method claims (claims 11-36) from consideration. Ex. 1002 at 207.

58. I was informed that after several prior art rejections, including by U.S. Patent No. 5,858,873 (“*Vitkavage*,” Ex. 1008), and claim amendments by the Applicant, the PTO eventually allowed the claims. *Id.*, 252-61. I also understand that during prosecution, the Examiner did not uncover prior art that would have disclosed the same claim elements he believed were missing from the art of record. I was informed that during prosecution, the Applicant distinguished the pending claims over *Vitkavage* by arguing *Vitkavage* does not disclose “said first film being formed on said second film” ([1.4] and [5.5]) and “said first film containing nitrogen in a smaller content than that of said second film” ([1.6] and [5.7]) as recited in the independent claims. However, I believe that a POSITA would have understood that these claim elements are disclosed, for example, in *Zhang*, as shown in the annotated FIG. 8 of *Zhang* below, which teaches a two-layer diffusion barrier including a top, first film 32 (in blue) formed on a bottom, second film 22 (in red). *Zhang* teaches the “nitrogen percentage for the second portion (32) is lower than the nitrogen atomic percentage for the first portion (22).” Ex. 1004, Abstract.

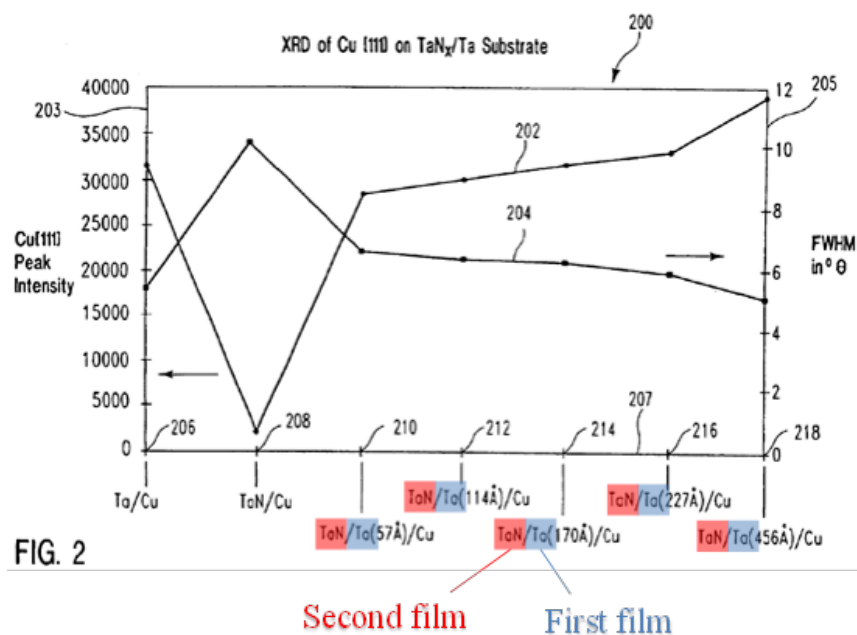


Annotated FIG. 8 of *Zhang* (Ex. 1004)

59. I understand that in *Zhang*, the “deposition [i.e., depositing] of the two films 22 and 32 is typically performed as one sequence during a single evacuation cycle,” where nitrogen is applied during sputter deposition of the bottom, second film 22 and then the nitrogen gas is turned off during the deposition of the top, first film 32 of the diffusion barrier. Ex. 1004, 3:37-38. As a result, the first film 32 contains a smaller nitrogen content than the second film 22. *Compare* Ex. 1004, 3:39-41 (film 22 contains TaN close to its stoichiometric composition, i.e., one-to-one atomic Ta to atomic nitrogen, which is 50 atomic percent nitrogen) *with id.*, 3:53-54 (film 32 contains 0-30 atomic percent nitrogen); *see also id.*, FIG. 4. The terminology in *Zhang* is slightly different from that in the ’324 patent. The *first* film in the ’324 patent corresponds to the *second* portion of the first conductive film in *Zhang*, while the *second* film in the ’324 patent corresponds to the *first*

portion of the first conductive film in *Zhang*. But these semantic differences are irrelevant.

60. I believe a POSITA would have understood that these elements are also disclosed in *Ding*, as shown in the annotated FIG. 2 of *Ding* below, which teaches a two-layer diffusion barrier structure with a top tantalum layer (in blue) overlying a bottom tantalum nitride layer (in red). See, e.g., Ex. 1005, 3:33-34 (“a layer of Ta overlying a layer of TaN_x”), 7:1-29, Abstract, 4:66-5:1 (“The TaN_x/Ta barrier layer structure”), FIG. 2.



Annotated FIG. 2 of *Ding* (Ex. 1005)

61. I understand that in *Ding*, “[t]o form the TaN_x/Ta barrier layer structure, a tantalum target cathode 110 was used,” where “[d]uring the formation of the TaN_x first layer, . . . [n]itrogen gas was also fed into vacuum chamber 117”

and “[s]ubsequent to application of the TaN layer, the nitrogen gas was shut off” to form “a . . . layer of tantalum . . . over the TaN layer.” Ex. 1005, 6:64-7:28. As a result, the first film 32 contains a smaller nitrogen content than the second film 22.

62. Further, I was informed that the claims were allowed after Applicant argued that U.S. Patent No. 5,668,411 to Hong et al. (“*Hong*”, Ex. 1009) does not disclose “said first film in direct contact with said second film” ([1.5] and [5.6]) as recited in the independent claims. Again, I believe that this claim element is disclosed in prior art, such as *Zhang*, which, to my knowledge, was not considered by the Examiner during prosecution. *See, e.g.*, Ex. 1004, FIG. 8 (annotated above, showing first film 32 in direct contact with second film 22).

63. I also believe that this claim element is disclosed in *Ding*, which, to my knowledge, was not considered by the Examiner during prosecution. *See, e.g., id.*, 3:33-34 (“We have developed a barrier layer structure comprising a layer of Ta overlying a layer of TaN_x”), 7:21-29 (describing the formation of the second layer directly on the first layer, whereby “[s]ubsequent to application of the TaN layer, the nitrogen gas was shut off” to form the Ta layer), 4:66-5:1 (“TaN_x/Ta barrier layer structure”), FIG. 2 (annotated above).

VIII. LEVEL OF ORDINARY SKILL

64. In my view, a person of ordinary skill in the art at the time the application leading to the '324 patent was filed would have an equivalent of a

Master of Science degree from an accredited institution in electrical engineering, materials science, or physics, or the equivalent, a working knowledge of semiconductor processing technologies for integrated circuits, and at least two years of experience in semiconductor processing analysis, design, and development. Additional graduate education could substitute for professional experience, and significant work experience could substitute for formal education.

65. I was at least a person of ordinary skill in the art at the time the application leading to the '324 patent was filed.

IX. CLAIM CONSTRUCTION

66. I was informed by counsel that the claims in the '324 patent should be understood based on their broadest reasonable construction in light of the patent specification for purposes of this *inter partes* review proceeding. Unless otherwise noted, my opinions in this declaration are consistent with the broadest reasonable construction of the claims to a person of ordinary skill in the art when the application leading to the '324 patent was filed.

X. ANALYSIS

A. Overview of the Prior Art

67. In my opinion, the '324 patent was not the first to recognize problems associated with single-layer barriers for preventing diffusion of copper and was not the first to suggest a multi-layer solution. The specification recognized a desire for

a diffusion barrier “having a high barrier characteristic of preventing copper diffusion and high adhesion to copper.” Ex. 1001, 3:47-49; *see also id.*, 2:12-15. On the one hand, the ’324 patent specification acknowledged that a barrier layer formed only of a crystalline metal film, such as a crystalline β -Ta (002) film, was known to provide “good adhesion” and “rich crystal orientation” (e.g., allowing a copper film to grow with good adhesion), but would serve as a poor barrier to copper diffusion. *Id.*, 3:14-20. This is because in such crystalline barrier films (or more accurately large grain polycrystalline films with dendritic structures), the films have grain boundaries extending from the top to the bottom of the films, which can act as high diffusivity pipelines for allowing copper to diffuse from the copper interconnects to underlying layers and the silicon substrate. In contrast, amorphous films with no grain boundaries, or tiny grains where the grain boundaries do not provide continuous pathways from the top to the bottom, act as better diffusion barriers. *Id.* On the other hand, a diffusion barrier formed only of an amorphous metal nitride, while providing a better barrier to copper diffusion since it “does not have the [grain-boundary] paths through which copper is diffused,” would suffer from poor adhesion, since “copper crystallinity and adhesion to copper are degraded” using an amorphous layer. *Id.*, 3:21-33.

68. I understand that, in view of these problems, the ’324 patent claims a two-layer diffusion barrier comprising overlying crystalline and amorphous films

with different nitrogen contents. *See, e.g., id.*, claims 1 and 5. In this structure, the bottom film of the barrier (substrate side) may be a previously-known amorphous metal nitride film, such as tantalum nitride, and the top film (copper side) may be a previously-known crystalline metal film containing less nitrogen than the bottom film. As I discuss below, both the problems with known diffusion barriers and the solution described in the '324 patent were already known in the prior art.

1. *Zhang*

69. In forming my opinions, I considered U.S. Patent No. 5,893,752 to Zhang et al., which discloses a “first conductive film” that serves as a multi-layer diffusion barrier relative to a “second conductive film” that includes mostly copper. Ex. 1004, Abstract. The first conductive film in *Zhang* is a two-layer diffusion barrier film having top and bottom portions 32 and 22, such that the bottom film 22 lies closer to the substrate than the top film 32.⁴ *Id.* According to *Zhang*, a “combination of portions (22 and 32) within the first conductive film provides a good diffusion barrier (first portion) and has good adhesion (second portion) with the second conductive film (54 and 64).” *Id.*

⁴ *Zhang* refers to the same thin films 22 and 32 as either “portions” or “films.” *See, e.g.,* Ex. 1004, Abstract (“portions (22 and 32)”), 3:37 (“films 22 and 32”).

70. In *Zhang*, the top (32) and bottom (22) films are tantalum-based films with different nitrogen contents. *Id.*, 3:22-23. The “nitrogen percentage for the second portion (32) is lower than the nitrogen atomic percentage for the first portion (22).” *Id.*, Abstract. In other words, *Zhang* recognized the same problems and the same two-layer solution as the ’324 patent. Indeed, *Zhang* meets every claim element of the ’324 patent, except it does not expressly mention the crystalline or amorphous nature of the films 22 and 32 disclosed for use in the diffusion barrier.

71. Nevertheless, in my opinion, a POSITA as of the filing date of the ’324 patent would have understood that *Zhang*’s process of forming the top film 32 suggests the top film 32 is more likely to be a crystalline film than bottom film 22, which is more likely to be amorphous. *Zhang* discloses that when the top film 32 is formed, “the substrate [is] biased at approximately negative 75 to negative 80 volts.” *Id.*, 3:44-47. Applying a negative bias to the substrate during a sputter-deposition process causes positive ions like argon or nitrogen in the plasma to hit the substrate with higher bombarding energy, i.e., higher kinetic energy. When these ions hit the surface of the substrate, they transfer some of their kinetic energy to adatoms (atoms previously arriving at and lying on the surface of the substrate), such as Ta adatoms. As a result, the adatoms receive more energy from the ions and have a higher mobility. Adatoms with a higher mobility will more likely move

to lattice sites in the film being formed, i.e., the adatoms will more likely be arranged as they are in a crystalline film. Therefore, a bias applied to the substrate, like that in *Zhang*, makes it easier to form a crystalline film 32 which corresponds to the first film in '324.

2. *Ding*

72. I also considered U.S. Patent No. 6,887,353 to Ding et al., which is directed to the same problems and solution as the '324 patent and *Zhang*, and explicitly addresses the crystalline/amorphous nature of the top and bottom films in the diffusion barrier. Ex. 1005, 3:33-34 (“We have developed a barrier layer structure comprising a layer of Ta overlying a layer of TaN_x ”). *Ding* discloses a two-layer “ TaN_x /Ta barrier structure” that “provides both a barrier to the diffusion of a copper layer deposited thereover, and enables the formation of a copper layer having a high $\langle 111 \rangle$ crystallographic content so that the electromigration resistance of the copper is increased.” Ex. 1005, Abstract. The diffusion barrier in *Ding* may consist of an amorphous tantalum nitride bottom film for preventing copper diffusion, (Ex. 1005, Abstract), and a crystalline tantalum top film for “easy wetting of the tantalum surface by the copper,” i.e., providing good adhesion to the copper layer, and “depositing of a copper layer having a high $\langle 111 \rangle$ crystal orientation” (Ex. 1005, 8:1-4).

73. As I note above, the bottom film of the two-layer diffusion barriers in both *Zhang* and *Ding* consists of a tantalum nitride (TaN_x) film, which *Ding* teaches may be an amorphous thin film. Ex. 1005, Abstract. The TaN_x film in *Zhang* is “close to the stoichiometric composition (TaN),” such that x equals one using the TaN_x nomenclature. Ex. 1004, 3:39-41; *see also id.*, 3:10-12 (“The tantalum nitride film 22 typically includes 33 to 50 atomic percent nitrogen with the balance essentially being tantalum”). *Ding* discloses a similar bottom “ TaN_x layer, where x ranges from about 0.1 to about 1.5, is sufficiently amorphous to prevent the diffusion of copper into the underlying substrate, which is typically silicon or a dielectric such as silicon dioxide.” Ex. 1005, Abstract. Other prior-art references, such as Holloway et al., “Tantalum as a diffusion barrier between copper and silicon: Failure mechanism and effect of nitrogen additions,” *Journal of Applied Physics*, vol. 71, no. 11, pages 5433-5444 (1992) (“*Holloway*,” Ex. 1006) and *Sun*, further describe properties of various Ta-based diffusion barrier layers at different nitrogen contents. *See, e.g.*, Ex. 1006, Abstract; Ex. 1007, Abstract.

74. *Zhang* discloses an embodiment in which the top film of the two-layer diffusion barrier is a “tantalum-rich tantalum nitride film” that has an upper surface

which is “substantially pure tantalum.” Ex. 1004, 3:54-57.⁵ Likewise, the top film of the barrier in *Ding* is also a tantalum layer, which *Ding* teaches is a crystalline film with a <002> crystalline orientation. Ex. 1005, 8:1-4. In my opinion, a POSITA reading *Ding* at the time of the ’324 patent’s filing date would have understood that the top tantalum film in *Ding* could contain a small percentage of nitrogen therein and still provide a “substantially pure tantalum” surface to deposit copper, as taught in *Zhang*. Indeed, the sputtering process described in *Ding* suggests the top tantalum film would contain at least a small amount of nitrogen, e.g., from residual nitrogen in the vacuum chamber after the nitrogen feed gas was turned off following the deposition of the bottom tantalum nitride (TaN_x) film. The POSITA also would have found it obvious to modify the top tantalum film in *Ding* to purposely add a small content of nitrogen therein, as taught in *Zhang*, because adding nitrogen to the tantalum film would provide well known benefits to the diffusion barrier, including better polishing characteristics (*see, e.g.*, Ex. 1019, at 12-13, Table 1; Ex. 1021, Table I), lower resistivity (*see, e.g.*, Ex. 1015, Table 1), and more effective blocking of copper diffusion for *Ding*’s diffusion-barrier structure (*see, e.g.*, Ex. 1023, at 8), as discussed in more detail below. In my

⁵ FIG. 4 in *Zhang* illustrates the atomic percentage of nitrogen in the top film 32 as a function of distance from its exposed surface. Ex. 1004, 3:50-53, FIG. 4.

opinion, modifying the top tantalum film in *Ding* to include nitrogen in view of *Zhang* would result in a two-layer barrier structure satisfying the claims of the '324 patent.

75. In view of the foregoing, and further in view of the reasons to combine *Zhang* and *Ding* I describe below, I believe it would have been obvious to a POSITA at the time of the '324 patent that the two-layer diffusion barrier consisting of a crystalline Ta film and an amorphous TaN_x film in *Ding* would have been usable as the two-layer diffusion barrier in *Zhang*, as both prior-art references teach the same diffusion-barrier structure for the same purpose of preventing copper diffusion and providing good adhesion to a copper layer using Ta-based thin films fabricated using similar sputtering deposition techniques. Put another way, in my opinion, a POSITA would have been motivated to modify *Zhang* to ensure the top film (32) of the diffusion barrier is crystalline and the bottom film (22) is amorphous given the teachings of *Ding*. It is also my opinion that a POSITA would have been motivated to modify *Ding* to ensure the top, crystalline Ta film of the diffusion barrier contains a small amount of nitrogen relative to the bottom TaN_x film in view of the teachings of *Zhang*.

3. Sun

76. I also considered the article “Properties of reactively sputter-deposited Ta-N thin films” by Sun et al., which teaches particular reasons why an amorphous

tantalum nitride film is desirable as a diffusion barrier. *Sun* discloses properties of Ta-N sputter-deposited thin films over a range of different compositions for use as a diffusion barrier between silicon and copper layers (*see, e.g.*, Ex. 1007 at 9, Abstract), and particularly that an amorphous film is a better barrier than a crystalline film because the amorphous film is “absen[t] of fast diffusion paths” *id.*, 9. The films range in composition from zero to 60 atomic percent (“at.%)” nitrogen. *See, e.g.*, Ex. 1007, Abstract, FIG. 3. As shown in FIG. 3, for example, *Sun* discloses that Ta-N films with low nitrogen concentrations (*e.g.*, below 10 at. %) are deposited as crystalline body-centered-cubic (bcc) films. *Id.*

B. I believe that the combined teachings of *Zhang* and *Ding* render claims 1-3, 5-7, and 9 obvious

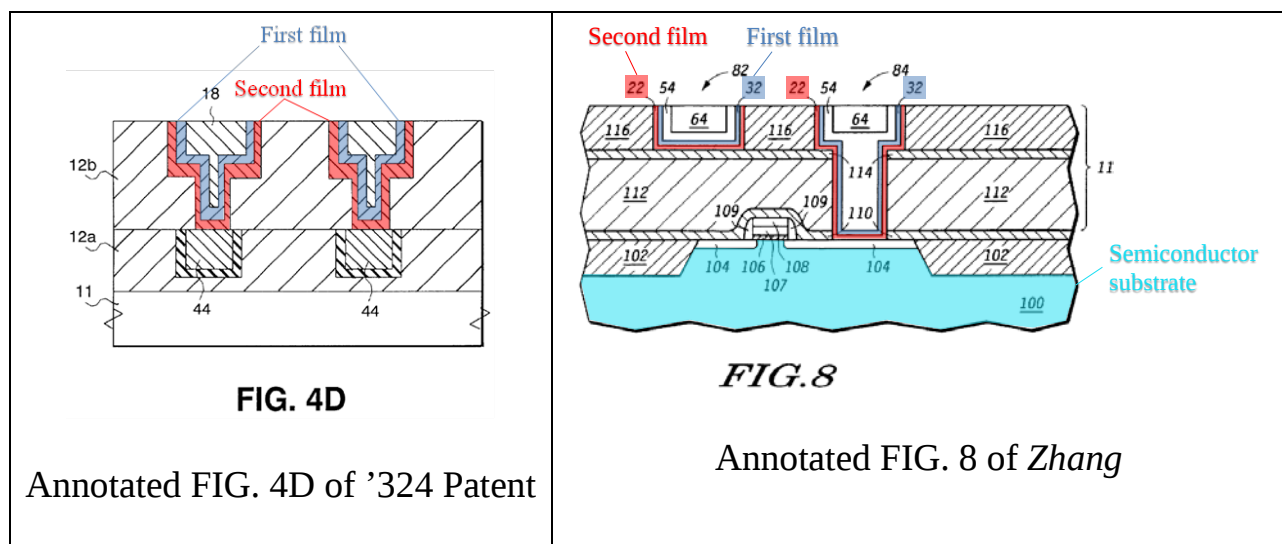
1. Claim 1 is obvious

77. It is my opinion that each element of claim 1 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*.

a) [1.0] *Zhang* discloses “A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films”

78. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses a barrier film (“first conductive film (22 and 32)”) preventing diffusion of copper (*see e.g.*, Abstract, “a good diffusion barrier”) from a copper wiring layer (“second conductive film (54 and 64) includ[ing] mostly copper”). Ex. 1004,

Abstract. *Zhang* discloses the barrier film (22 and 32) is formed on a semiconductor substrate 100. *Id.*, Abstract, 2:43-44, and FIG. 8. *Zhang* further discloses that the barrier film comprises a multi-layered structure of first (32) and second (22) films. *Id.*, Abstract, and FIG. 8. Figure 4D of the '324 patent and FIG. 8 of *Zhang* below (with added annotations) show the similarities between the structures.



- b) [1.1] and [1.2] *Zhang* in view of *Ding* discloses “said first film being composed of crystalline metal containing nitrogen therein” and “said second film being composed of amorphous metal nitride”

79. In my opinion, this claim element would have been obvious to a POSITA at the time of the '324 patent based on *Zhang* in view of *Ding*. *Zhang* discloses the first film (top film 32) is composed of a metal, tantalum, containing nitrogen therein as required in claim element [1.1]. *See, e.g., id.*, 3:14-16, (“The

substrate is then further processed to form a *tantalum-rich tantalum nitride film 32* that overlies the tantalum nitride film 22 as shown in FIG. 3”) (emphasis added); *see also id.*, FIGS. 3 and 4.. Although *Zhang* uses the term “tantalum-rich tantalum nitride” rather than a tantalum metal “containing nitrogen,” I understand that the specification includes embodiments in which the claimed “metal containing nitrogen therein” is a tantalum-rich tantalum nitride. *See, e.g.*, Ex. 1001, 12:66-67 (referring to the “crystalline metal film containing nitrogen therein” as including a mixture of β -Ta and $\text{TaN}_{0.1}$, i.e., which is a tantalum-rich tantalum nitride); *see also* Ex. 1002 at 220 (Applicant stating that “first film 16 is composed of $\text{TaN}_{0.1}$ which is called nitrogen-containing α -Ta, or a combination of $\text{TaN}_{0.1}$ and β -Ta . . . [t]hat is, the first film 16 is composed of crystalline *metal containing nitrogen*”) (emphasis added).

80. FIG. 4 shows the amount of nitrogen in the top film 32 of the diffusion barrier in *Zhang* as “a plot of concentration (in atomic percent) as a function of the distance from the exposed surface” of the film 32. Ex. 1004, 3:48-53. As shown in FIG. 4, the atomic percent of nitrogen in the “tantalum-rich tantalum nitride film” 32 is very small at the exposed surface and increases as a function of distance up to the interface with bottom film 22 (designated with a dotted line). In the top film 32, and as shown in FIG. 4, the “tantalum-rich tantalum

nitride film has a range of approximately 0-30 atomic percent nitrogen.” *Id.*, 3:53-54.

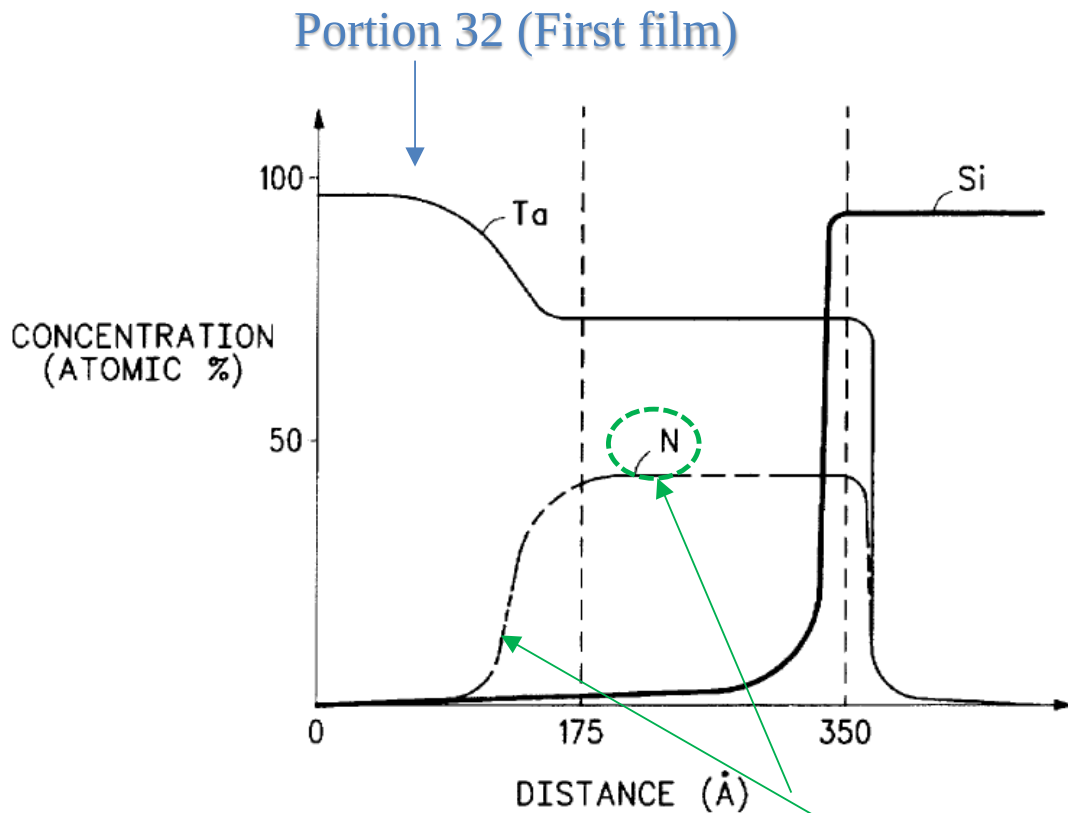


FIG.4 First film contains nitrogen

Annotated FIG. 4 of *Zhang*

81. *Zhang* further discloses that the second film (bottom film 22) is composed of tantalum nitride, which is a “metal nitride film” as recited in claim element [1.2]. For example, *Zhang* discloses “tantalum nitride film 22 is then deposited over the substrate within the openings 12.” Ex. 1004, 3:9-10; *see also id.*, 3:22-23 (disclosing that the “formation of the tantalum nitride and tantalum-rich tantalum nitride films 22 and 32 are formed as follows.”). FIG. 4 shows the

atomic percent of nitrogen through the depth of tantalum nitride film 22 as a function of distance, again measured relative to the exposed surface of top film 32.

Id., FIG. 4.

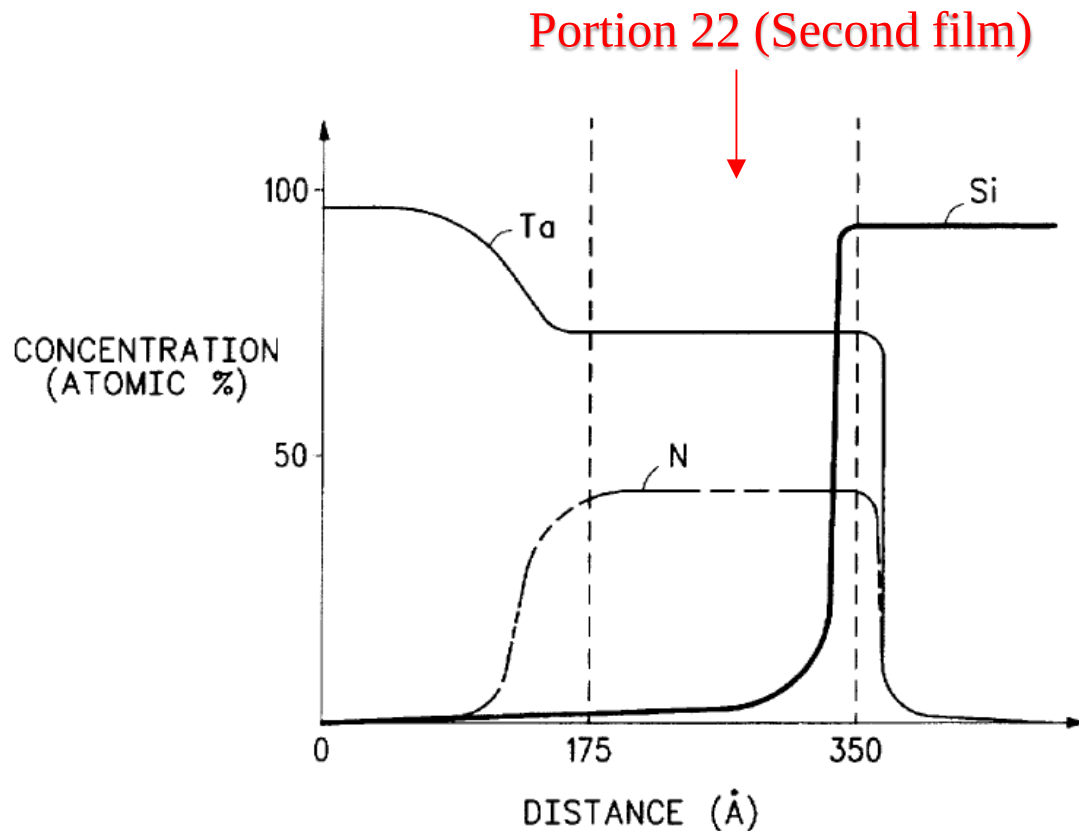


FIG. 4

Annotated FIG. 4 of *Zhang*

82. I believe the claimed crystalline and amorphous first and second layers in claim 1 are obvious over *Zhang* in view of *Ding*.

83. In my opinion, *Zhang* discloses every element of claim 1 of the '324 patent, except it does not explicitly disclose that top portion 32 is a “crystalline”

metal film containing nitrogen therein or that bottom portion 22 is an “amorphous” metal nitride film. *Ding* teaches this limitation in combination with *Zhang*, and I believe it would have been obvious to a POSITA to combine *Zhang* and *Ding* to ensure that the top, tantalum-rich tantalum nitride film 32 was crystalline and the bottom, tantalum nitride film 22 was amorphous.

84. *Zhang* discloses a two-layer barrier structure having a bottom film 22 composed of tantalum nitride and a top film 32 composed of tantalum-rich tantalum nitride, and *Ding* similarly discloses a two-layer barrier structure comprising a bottom film composed of TaN_x (i.e., tantalum nitride) and a top film composed of tantalum metal. *See, e.g.*, Ex. 1005, Abstract. In this two-layer barrier structure, *Ding* discloses the desirability of using an amorphous TaN_x layer as the bottom layer, so the TaN_x is “*sufficiently amorphous* to prevent the diffusion of copper into underlying silicon or silicon oxide surfaces” *Id.*, 3:39-41 (emphasis added). This disclosure in *Ding* is consistent with the ’324 patent’s Background of the Invention, which similarly discloses that amorphous TaN “does not have paths through which copper is diffused unlike the crystalline metal film 5 illustrated in FIG. 2.” Ex. 1001, 3:21-28; *see also* Ex. 1004, 5:50-51 (“The tantalum nitride film is a good barrier”).

85. *Ding* also discloses the desirability of using a crystalline metal film “having a tantalum <002> crystalline orientation” as a top film in the two-layer

diffusion barrier because the crystalline orientation “enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystal orientation.” Ex. 1005, 8:1-4. A POSITA would have understood this to mean that because the crystalline top film in *Ding* provides “easy wetting” by copper having a high <111> crystal orientation, it facilitates growth of such a copper wiring layer and improves adhesion of the top film to that copper layer. *See, e.g.*, Ex. 1004, 2:37-40 (teaching the top film (second portion) of the barrier has “good adhesion”). *Ding* further teaches that “a copper layer having a high <111> crystallographic content,” which is deposited over the barrier layer, is desirable because it increases “copper electromigration resistance” (*id.*, Abstract, 3:36-38, 5:1-3), and copper electromigration “can result in conductor failure . . . [and] severely limit the reliability of the circuit” (*id.*, 2:10-21). *Zhang* also acknowledges this advantage. Ex. 1004, 5:60-62 (“Further, embodiments of the present invention reduce the effects of electromigration”).

86. In my opinion, a POSITA would have found it obvious to combine the teachings of *Zhang* and *Ding*. As I describe above, *Zhang* in view of *Ding* teaches the sub-element of claim 1 reciting a crystalline first layer and an amorphous second layer of the diffusion barrier. In my opinion, it would have been obvious for a POSITA to combine *Zhang* and *Ding* for at least the following reasons, each one of which I understand is sufficient: (1) *Zhang* suggests the formation of a

diffusion barrier with a crystalline top film and an amorphous bottom film in view of *Ding*; (2) a POSITA would have found it obvious to combine *Zhang* and *Ding* to achieve the predictable benefits of such a combination; and (3) the combination of *Zhang* and *Ding* simply applies known techniques to yield predictable results.

87. In my opinion, *Zhang* suggests the formation of crystalline top and amorphous bottom films in view of *Ding*. I believe that A POSITA at the time of the '324 patent's filing date would have understood that *Zhang*'s description of the top and bottom films 32 and 22 suggests the top film would be crystalline and the bottom film amorphous, especially in view of *Ding*. *Zhang* teaches a sputter deposition process that applies a substrate bias and turns off the nitrogen feed gas when forming the top film 32 but not the bottom film 22. *See, e.g.*, Ex. 1004, 3:37-47. In my opinion, the POSITA would have understood that applying a substrate bias for only the top film and adding more nitrogen in the bottom film would promote growth of a crystalline top film and amorphous bottom film as this claim element requires.

88. First, I note that *Zhang* teaches applying a substrate bias only during the sputtering deposition of the top film 32, and not during the formation of the bottom film 22. *Compare* Ex. 1004, 3:39-41 ("no biasing of the substrate" when forming film 22) *with* 3:44-47 ("In forming film 32 . . . the substrate becomes biased at approximately negative 75 to negative 80 volts"). In my opinion, it was

well known at the time to a POSITA that applying a substrate bias during a sputtering process increases adatom mobility at a surface of the substrate and increases the likelihood that the adatoms will migrate to crystalline lattice sites, thus promoting formation of a crystalline film, such as the top film 32 in *Zhang*. See, e.g., Duan et al., “Magnetic Property and Microstructure Dependence of CoCrTa/Cr Media on Substrate Temperature and Bias,” IEEE Transactions on Magnetics, Vol. 28, No. 5, September 1992 (Ex. 1017), at 17 (“substrate biasing during sputtering seem[s] to have the . . . effect of increasing the adatom mobility and promoting a continuous, closely-packed-grains structure in the film”).

89. I believe that the POSITA would have recognized that *Zhang* suggests applying a substrate bias in forming the top film 32 to promote the formation of a crystalline film, while removing the substrate bias in forming bottom film 22 would not promote crystalline growth. And because the application of a substrate bias was intentionally included for top film 32 and omitted for bottom film 22 in *Zhang*, the POSITA would have understood the top film 32 to be crystalline and the bottom film 22 amorphous.

90. My belief is further supported by the teaching in *Zhang* that the bottom film 22 has a much larger atomic percentage of nitrogen (see, e.g., Ex. 1004, FIG. 4 and 3:10-12), and it was well known to a POSITA that a high content of nitrogen would interrupt formation of periodic crystalline structures, resulting in

an amorphous film. In my opinion, the POSITA would have further appreciated that a high percentage of nitrogen can promote the formation of amorphous alloys in tantalum films. *See, e.g.*, Ex. 1007 at 9 (“nitrogen can [] promote the formation of amorphous metallic alloys with most early transition metals”). Accordingly, the POSITA would have understood *Zhang* suggests the bottom tantalum-nitride film 22 is likely amorphous due to its high nitrogen content. *See, e.g.*, Ex. 1004, 3:39-41 (“the tantalum nitride film 22 is close to the stoichiometric composition (TaN),” i.e., close to 50% nitrogen), 3:10-12.

91. Moreover, in my opinion, nothing in the existing sputtering-deposition process in *Zhang* would have prevented the top barrier film 32 from being crystalline. *Zhang* already discloses a sputtering process that creates the film 32 with an upper surface that is “substantially pure tantalum and has essentially no nitrogen atoms,” which is essentially a tantalum layer like the crystalline top film in *Ding*. Ex. 1004, 3:54-57, FIG. 4 (nitrogen content approaching zero at the exposed surface of film 32); Ex. 1005, 3:33-34, 7:66-8:4. A POSITA at the time of the '324 patent's filing date would have understood that a small amount of nitrogen in a tantalum film would not preclude that film from being crystalline. *See, e.g.*, Ex. 1006, t 9 (disclosing both a Ta film and a TaN_x film with only 5 atomic percentage nitrogen have the same crystalline phase, β -Ta: “a 0.25% N₂/Ar mixture produced a film with 5 at.% nitrogen content” and “[e]lectron-diffraction

patterns taken from through-foil transmission electron microscopy (TEM) specimens allowed the identification of β -Ta in [this] case”; “[t]he Ta film deposited in pure Ar was also found to be β -Ta.”).

92. Finally, the POSITA would have found it obvious to form a crystalline top film 32 and an amorphous bottom film 22 in *Zhang* to achieve predictable advantages and yield predictable results, as demonstrated by *Ding*. These predictable advantages and results include better diffusion barrier characteristics, improved growth of a copper wiring layer, and improved adhesion of the top barrier film to that copper layer, as discussed in the sections below. *See, e.g.,* Ex. 1005, 3:33-36 (“We have developed a barrier layer structure comprising a layer of Ta overlying a layer of TaN_x which provides both a barrier to the diffusion of a copper layer deposited thereover, and enables the formation of a copper layer having a high <111> crystallographic content”); 8:1-4, Abstract.

93. Also, I believe that a POSITA would have found it obvious to combine *Zhang* and *Ding* to achieve predictable advantages. In my opinion, it would have been obvious to a POSITA to combine *Zhang* and *Ding* to ensure that the top, tantalum-rich tantalum nitride film 32 was crystalline and the bottom, tantalum nitride film 22 was amorphous because *Ding* explains the advantages of that arrangement. I believe that a POSITA would have used the teachings of *Ding* to form a crystalline top film 32 (i.e., the tantalum-rich tantalum nitride film) in the

diffusion barrier of *Zhang* to allow easy wetting of its exposed surface by the copper layers deposited above it (54 and 64), and to enable the deposition of the copper layers (54 and 64) with a high crystal orientation, which, in turn, would increase circuit reliability. Ex. 1005, 8:1-4; Abstract; 3:36-38; 5:1-3; 2:10-21. In my opinion, a POSITA would also have been motivated to combine the similar two-layer diffusion barriers taught in *Zhang* and *Ding* at least to incorporate the advantages of using amorphous and crystalline phases in the bottom and top layers as taught in *Ding*, thereby preventing diffusion of copper (via the amorphous layer) and improving adhesion to copper (via the crystalline layer) which are goals in both references. See, e.g., Ex. 1004, 5:48-62; Ex. 1005, 3:32-37.

94. In my opinion, it would have been obvious to a POSITA, in view of *Ding*, to make bottom film 22 of the diffusion barrier in *Zhang* amorphous to obtain the benefit of preventing diffusion of copper into the underlying silicon. *Id.*, 3:39-41. I believe that this is especially obvious because the function of bottom film 22 of *Zhang* is to “provide a good diffusion barrier” (Ex. 1004, Abstract and 2:37-39), and this function can be improved by using an amorphous tantalum nitride film as taught by *Ding*. Ex. 1005, Abstract (“The TaN_x layer . . . is sufficiently amorphous to prevent the diffusion of copper into the underlying substrate”).

95. I believe that the proposed combination also would have been obvious to a POSITA because *Zhang* and *Ding* both address two-layered, tantalum-based diffusion barriers for improving adhesion to copper films. For example, *Zhang* teaches that “tantalum nitride has adhesion problems with some types of copper films,” Ex. 1004, 1:33-34, and *Ding* discloses that adhesion to copper films can be improved using a crystalline orientation that “enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystal orientation.” Ex. 1005, 8:1-4. *See also, e.g.*, Ex. 1005, Abstract (“the copper may tend to dewet/delaminate from the barrier layer if the temperature is too high”), 8:4-7 “[a]lthough a higher temperature is required to dewet/delaminate a depositing copper layer from a Ta surface than from a TaN_x surface, copper delamination is a problem in some instances”).

96. In my opinion, because *Zhang* and *Ding* teaches that their respective diffusion barriers further provide the advantage of reducing electromigration of the copper layer, I believe a POSITA would have understood that the combination of these references would preserve this stated benefit. *Zhang* discloses that “embodiments of the present invention reduce the effects of electromigration.” Ex. 1004, 5:60-62. *Ding* similarly teaches a diffusion barrier that provides “improved electromigration resistance of the copper.” Ex. 1005, 1:10-14.

97. More generally, I believe that modifying the top and bottom films 32 and 22 of the two-layer diffusion barrier in *Zhang* in view of the top and bottom films in *Ding* also would have been obvious to a POSITA because both *Zhang* and *Ding* are directed to the specific area of improving diffusion barrier films in semiconductor devices with copper interconnects.

98. Also, I believe that the combination of *Zhang* and *Ding* applies known techniques to yield predictable results. In my opinion, any modifications of the two-layer barrier film of *Zhang* in view of the barrier film in *Ding* would have used well-known, common techniques, such as similar manufacturing processes to create the top and bottom films in the diffusion barrier. More particularly, *Zhang* and *Ding* use similar sputter-deposition techniques for forming the top and bottom films. See, e.g., Ex. 1004, 3:21-50; Ex. 1005, 6:63-7:29. In *Zhang*, the “deposition of the two films 22 and 32 is typically performed as one sequence during a single evacuation cycle” (Ex. 1004, 3:37-38), where the bottom TaN_x film 22 is sputter-deposited using a mixture of argon and nitrogen gases, then the nitrogen gas is terminated while the argon continues to maintain a plasma for sputter-depositing the top tantalum-rich tantalum nitride film 32 (*id.*, 3:41-47). Similarly, *Ding* discloses sputter depositing the bottom TaN_x film using a mixture of argon and nitrogen gases, then “[s]ubsequent to application of the TaN layer, the nitrogen

was shut off . . . and the argon gas feed was maintained” to deposit the top tantalum film. Ex. 1005, 6:64-7:29.

99. I believe that the proposed combination of *Zhang* in view of *Ding* would have yielded predictable results to a POSITA since the sputter-deposited films in both the diffusion barriers of *Zhang* and *Ding* provide good diffusion barrier characteristics and an improved interface between the diffusion barrier and a copper layer formed over it. *Zhang* teaches “[t]he combination of portions within the first conductive film provides a good diffusion barrier (first portion) and has good adhesion (second portion) with the second conductive film.” Ex. 1004, 2:37-40; *see also id.*, 5:49-53. Addressing these same diffusion and adhesion issues, *Ding* teaches a top crystalline film “enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystal orientation . . .” (Ex. 1005, 8:1-4), while a bottom amorphous film “[prevents] the diffusion of copper into underlying silicon or silicon oxide surfaces” (*id.*, 3:39-41).

100. In my opinion, the combination of *Zhang* and *Ding* would not produce unexpected results, but instead would behave exactly as a POSITA at the time would have predicted. *See, e.g.*, Ex. 1005, 3:39-41, 8:1-4 (teaching that crystalline metal layer enables the “easy wetting of the tantalum surface by the copper,” i.e., providing good adhesion to the copper layer, and “depositing of a copper layer having a high <111> crystal orientation,” while an amorphous layer “[prevents] the

diffusion of copper into the underlying substrate”); *see also* Ex. 1001 (teaching a copper film formed on a crystalline metal film “would have high adhesion and rich crystal orientation” but poor “barrier characteristic of preventing copper diffusion” while “amorphous TaN . . . does not have the paths through which copper is diffused unlike the crystalline metal film” and thus “would have high barrier characteristic of preventing copper diffusion”).

c) [1.3] *Zhang* discloses “said barrier film being constituted of common metal atomic species”

101. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses the barrier film being constituted of a common metal atomic species, namely, tantalum. For example, *Zhang* discloses that the first film (top portion 32) of the diffusion barrier film is composed of tantalum-rich tantalum nitride and the second film (bottom portion 22) of the barrier film is composed of tantalum nitride. *See, e.g.*, Ex. 1004, 3:22-23 (disclosing the “formation of the tantalum nitride and tantalum-rich tantalum nitride films 22 and 32 are formed as follows”), 3:9-16 (“A tantalum nitride film 22 is then deposited over the substrate and within the openings 12. . . The substrate is then further processed to form a tantalum-rich tantalum nitride film 32 that overlies the tantalum nitride film 22 as shown in FIG. 3”); *see also id.*, 3:48-62, FIG. 4.

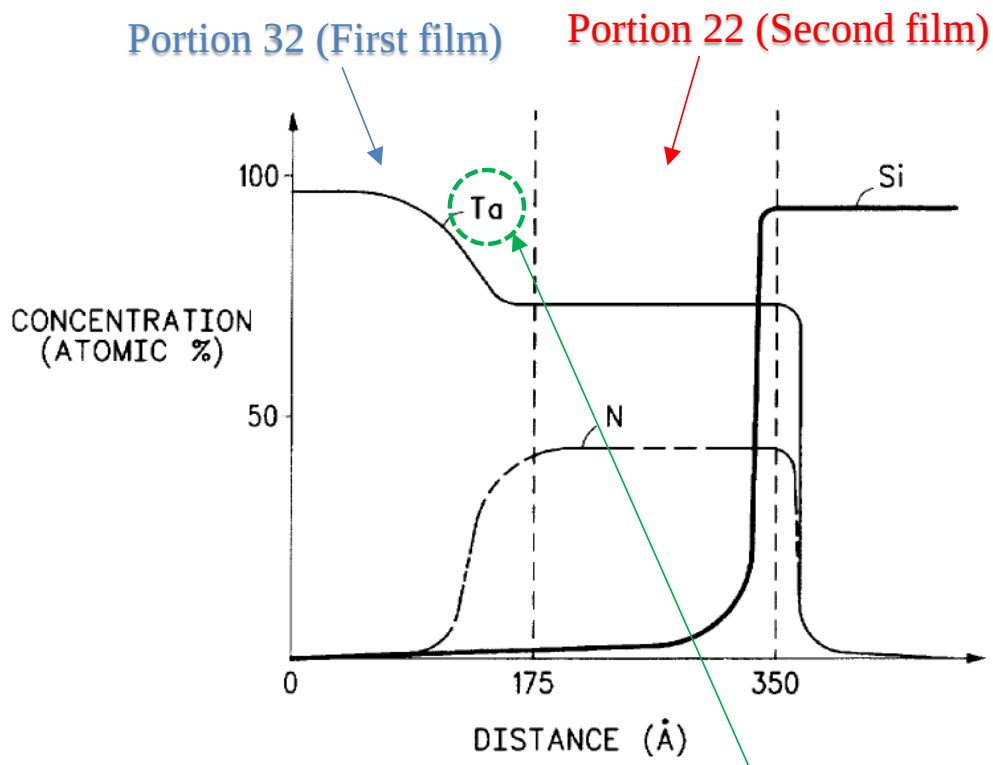


FIG. 4 Common metal atomic species

Annotated FIG. 4 of *Zhang*

d) [1.4] *Zhang* discloses “said first film being formed on said second film”

102. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses the first film (top portion 32) being formed on the second film (bottom portion 22) as required by this claim limitation. See, e.g., Ex. 1004, 3:14-16 (disclosing “a tantalum-rich tantalum nitride film 32 that overlies the tantalum nitride film 22 as shown in FIG. 3”); see also *id.*, FIG. 4 and FIG. 8.

(bottom portion 22) as required by this claim limitation. *See, e.g.*, Ex. 1004, 3:14-16 (disclosing “a tantalum-rich tantalum nitride film 32 that overlies the tantalum nitride film 22 as shown in FIG. 3”); *see also id.*, FIG. 4 and FIG. 8.

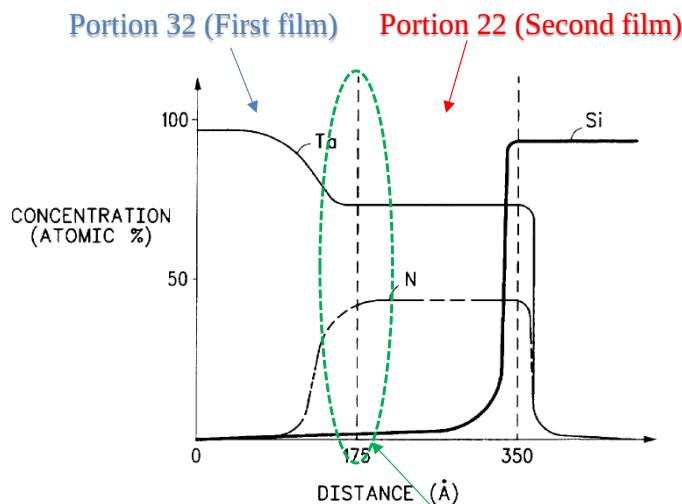


FIG. 4 First film in direct contact with second film

Annotated FIG. 4 of Zhang

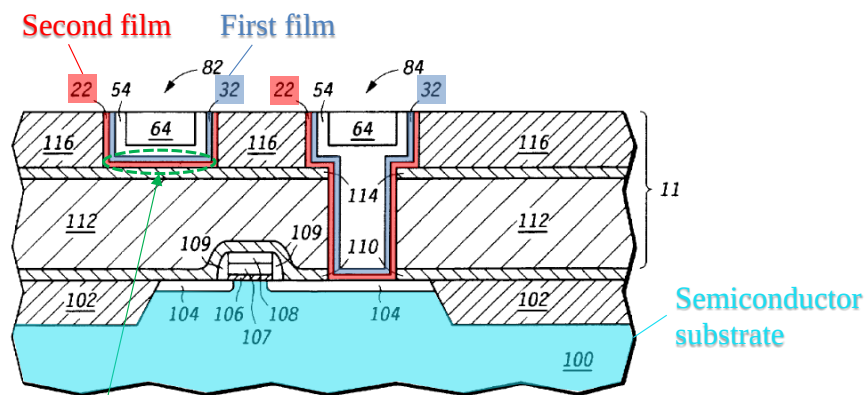


FIG. 8 First film in direct contact with second film

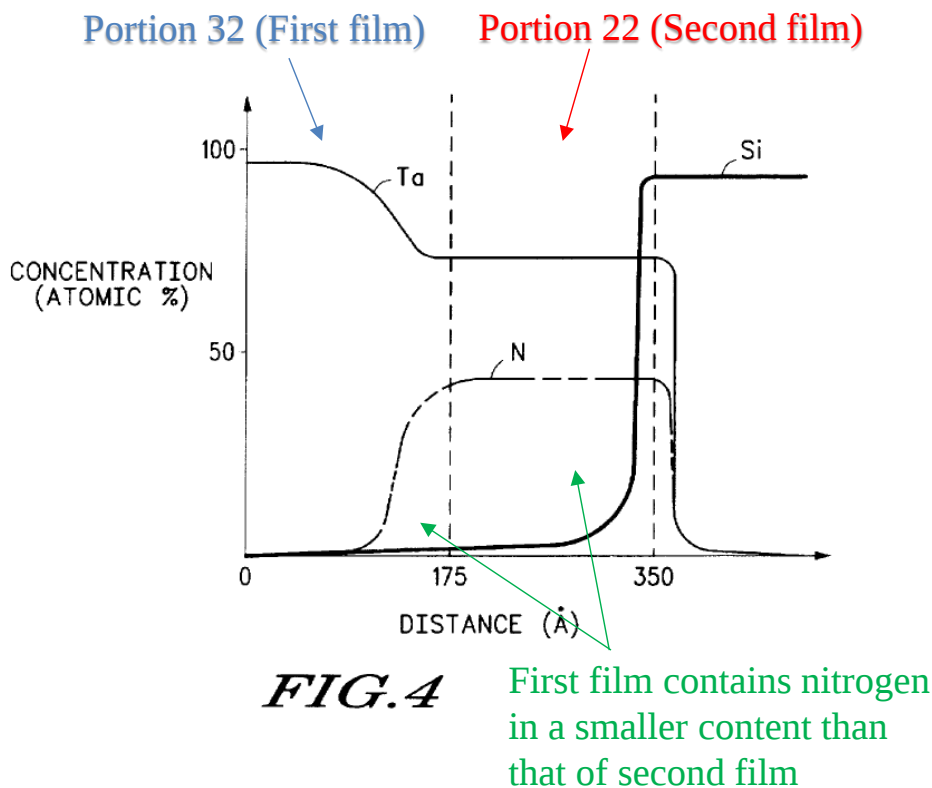
Annotated FIG. 8 of Zhang

f) [1.6] *Zhang* discloses “said first film containing nitrogen in a smaller content than that of said second film”

104. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses that first film 32 contains nitrogen in a smaller content than that of second film 22 in the two-layer diffusion barrier. For example, FIG. 4 of *Zhang* shows the concentration/atomic percentage of nitrogen is lower in the first film 32 than in the second film 22. Ex. 1004, FIG. 4. Further, *Zhang* discloses sputter-depositing both the first and second films 32 (top film) and 22 (bottom film) during the same evacuation cycle, such that second film 22 is deposited using a mixture of nitrogen and argon gases, but “[i]n forming film 32, the nitrogen-containing gas is terminated while the inert gas [i.e., argon] continues to flow.” *Id.*, 3:37-47. As a result of terminating the nitrogen gas when depositing the film 32, the first film 32 in *Zhang* will contain a smaller nitrogen content than that of the second film 22, thereby satisfying this claim element.

105. I was informed that during prosecution of the '324 patent, the Applicant stated that the first layer 16 in the patent “is composed of crystalline metal containing nitrogen at *10% or smaller*, and the second film 15 is composed of amorphous metal nitride containing nitrogen at *about 30%*,” and further that the “first layer 16 contains nitrogen in a *smaller content* than that of the second film 15.” Ex. 1002 at 220 (underline removed from original, italics added). In my

opinion, this same relationship is disclosed in FIG. 4 of *Zhang*, where the top film 32 contains nitrogen in a smaller content than that of the bottom film 22 as this claim element requires.



Annotated FIG. 4 of *Zhang*

2. Claim 2 is obvious

106. It is my opinion that each element of claim 2 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*.

- a) [2] *Zhang* discloses “The barrier film as set forth in claim 1, wherein said second film has a thickness in the range of 80 Angstroms to 150 Angstroms both inclusive”

107. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses that “[t]he combined thickness of the two films 32 and 22 is in a range of approximately 10 to 500 Angstroms, and typically is in a range of approximately 100 to 300 Angstroms.” Ex. 1004, 4:7-10. A preferred embodiment of *Zhang* suggests that the thickness of the bottom tantalum-nitride film 22 may be approximately the same as the thickness of the top tantalum-rich tantalum nitride film 32. *Id.*, 4:1-10 (“In one particular embodiment, the time period when the nitrogen-containing gas flows and biasing is off (film 22) is approximately equal to the time period when the nitrogen-containing gas flow is terminated and the biasing is on (film 32).”); *see also id.*, FIG. 4 (illustrating approximately equal thicknesses of the first and second films).

108. Because *Zhang* discloses a combined thickness of the films 32 and 22 in the range of 10 to 500 angstroms, and that the thickness of the films 32 and 22 may be approximately equal (*see, e.g., id.*, 4:1-5, FIG. 4), *Zhang* discloses the range of thicknesses for bottom film 22 would be approximately half of 10 to 500 angstroms, or 5 to 250 angstroms, which includes the claimed range of 80 to 150 angstroms. Even if the barrier in *Zhang* is constrained to using the “typical” combined thickness of films 32 and 22 in the range of 100 to 300 angstroms (Ex.

1004, 4:7-10), where the thickness of these films may be approximately equal, *Zhang* discloses the thickness range of film 22 is typically half of 100 to 300 angstroms, or 50 to 150 angstroms, which again includes the claimed range of 80 to 150 angstroms. In either case, the thickness range for the bottom TaN_x film 22 in *Zhang* discloses the entire range recited in claim 2.

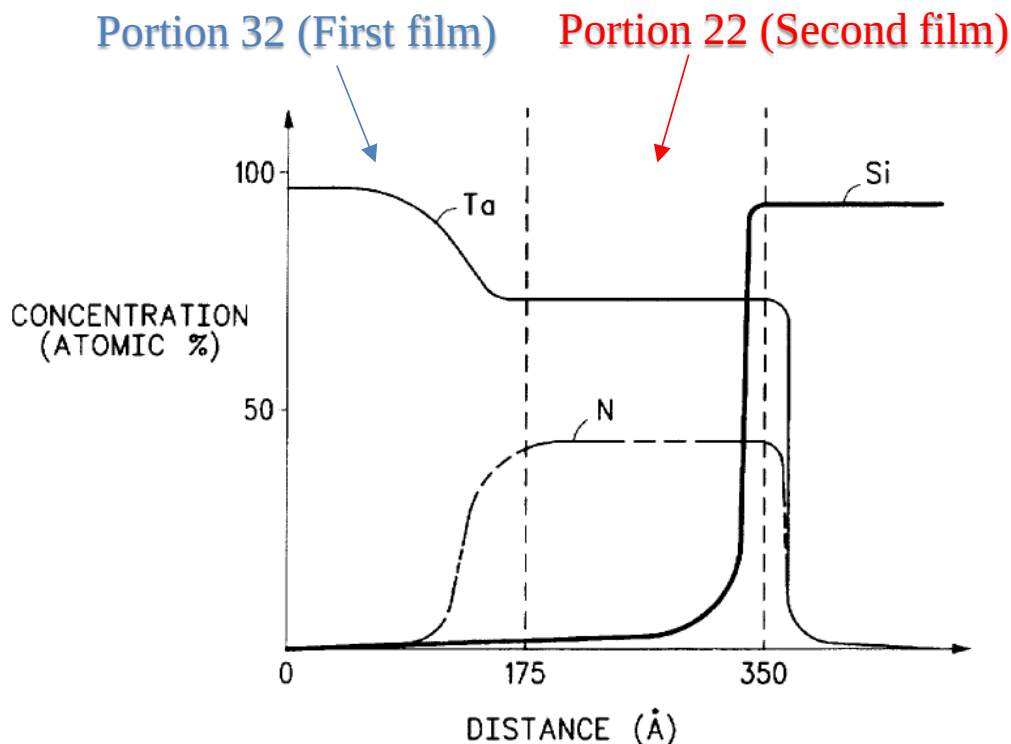


FIG. 4

Annotated FIG. 4 of *Zhang*

109. In my opinion, *Zhang*'s disclosed typical range of 50 to 150 Angstroms teaches the claimed range of 80 to 150 Angstroms with sufficient specificity because the ranges overlap for the most part, from 80 to 150 Angstroms, with the only non-lapping range from 50 to 80 Angstroms representing a small

percentage of the overall range. I understand that the only reason the '324 patent provides for having a second-film thickness in the range from 80 to 150 Angstroms is so that “barrier characteristic of preventing copper diffusion is ensured and adhesion with the underlying insulating film . . . is also ensured.” Ex. 1001, 13:51-54. But in my opinion, the patent contains no evidence that using a film with a thickness in the range of 50-80 Angstroms will fail to prevent copper diffusion or proper adhesion with the underlying insulating film.

110. In addition, I understand that *Ding* discloses that the bottom TaN_x film in its disclosed diffusion barrier has a thickness “from about 10 Å to about 300 Å,” which also contains the thickness range in claim 2. Ex. 1005, 4:34.

111. In my opinion, even if *Zhang* does not expressly disclose the claimed thickness range for the second film 22, which is a TaN_x film (Ex. 1004, 3:9-12, “tantalum nitride film 22 is then deposited”), the claimed thickness range would have been obvious to a POSITA in view of the thickness of the second TaN_x film disclosed in *Ding*. In my opinion, a POSITA would have been motivated to combine the teachings of *Zhang* with *Ding* for at least the same reasons I gave above.

3. Claim 3 is obvious

112. It is my opinion that each element of claim 3 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*.

- a) [3] *Zhang* discloses “The barrier film as set forth in claim 1, wherein said first film has a thickness in the range of 60 Angstroms to 300 Angstroms both inclusive”

113. In the embodiment shown in FIG. 4 of *Zhang*, the thickness of the first film (portion 32) is about 175 Angstroms. Ex. 1004, FIG. 4 (see dotted line showing transition between films 32 and 22 at 175 Å). Further, *Ding* discloses an embodiment where the top tantalum film has a thickness of 114 Å, which is within the claimed range for the first-film thickness. Ex. 1005, FIG. 2. *Ding* further discloses a first film composed of tantalum having a thickness “from about 5 Å to about 300Å,” which also includes the claimed range. Ex. 1005, 4:36. In my opinion, to the extent *Zhang* does not expressly disclose the claimed thickness range for the first film 32, which is a tantalum-rich tantalum nitride film (Ex. 1004, 3:14-16, “a tantalum-rich tantalum nitride film 32 that overlies the tantalum nitride film 22,” and 3:54-57, “the upper surface of the tantalum-rich tantalum nitride film is substantially pure tantalum”), I believe that it would have been obvious to a POSITA at the time to form the film 32 in *Zhang* with the claimed thickness range in view of the first film thickness disclosed in *Ding*. In my opinion, a POSITA

would have been motivated to combine the teachings of *Zhang* with *Ding* for at least the same reasons I gave above.

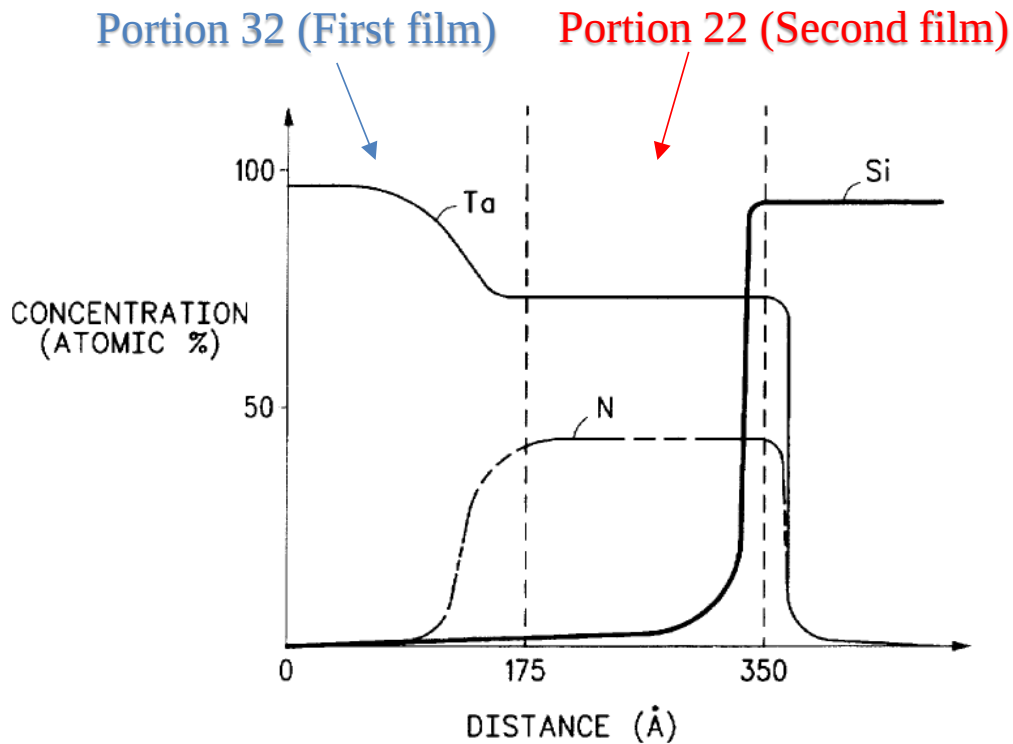


FIG. 4

Annotated FIG. 4 of *Zhang*

4. Claim 5 is obvious

114. It is my opinion that each element of claim 5 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*.

a) [5.0] *Zhang* discloses “A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate”

115. It is my opinion that *Zhang* teaches this claim element. I understand that Claim 5 differs from claim 1 only in that it recites a multi-layered wiring structure comprising the barrier film of claim 1. In contrast, claim 1 recites only the barrier film itself. As I explained in detail for [1.0], *Zhang* discloses a multi-layered wiring structure (see, e.g., Fig. 8) comprising a barrier film (“first conductive film (22 and 32)”), which provides “a good diffusion barrier” for a “second conductive film (54 and 64) includ[ing] mostly copper.” *Id.*, Abstract. *Zhang* discloses that the first conductive film is formed on semiconductor device substrate 100. *Id.*, Abstract (“first conductive film (22 and 32) over the substrate (100)”), 2:43-44, and FIG. 8.

b) [5.1] *Zhang* discloses “said barrier film having a multi-layered structure of first and second films”

116. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses that the barrier film has a multi-layered structure of first (portion 32) and second (portion 22) films. *Id.*, Abstract, and FIG. 8.

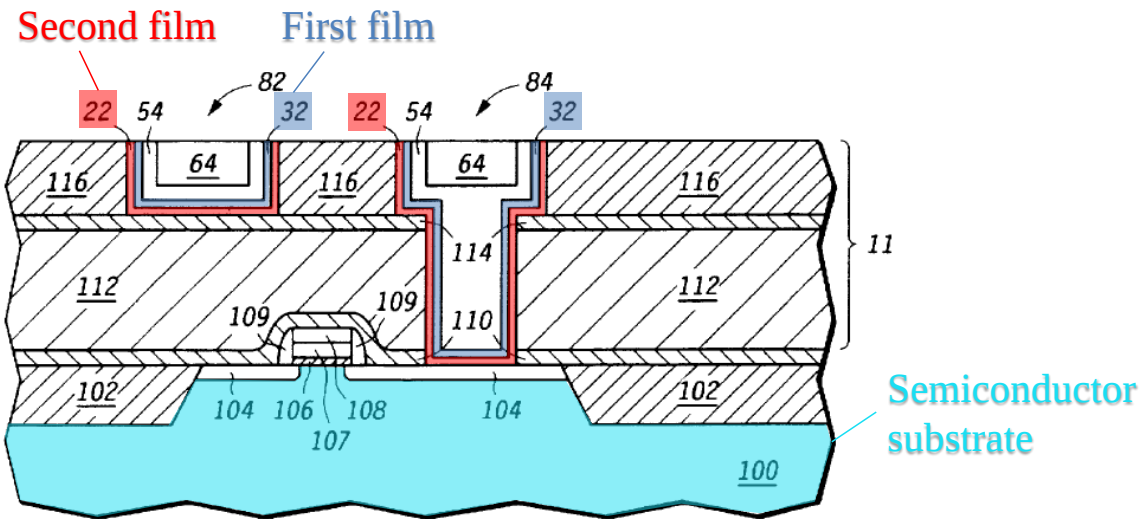


FIG. 8

Annotated FIG. 8 of *Zhang*

c) *Zhang* in view of *Ding* render obvious [5.2]-[5.7]

117. I believe that limitations [5.2]-[5.7] of claim 5, which are identical to limitations [1.1]-[1.6] of claim 1, are obvious in view of *Zhang* and *Ding* for at least the same reasons I gave above for [1.1]-[1.6].

5. Claim 6 is obvious

118. It is my opinion that each element of claim 6 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*. I believe that Claim 6, which is substantively similar to claim 2, is obvious in view of *Zhang* and *Ding* for at least the same reasons I gave above for claim 2.

6. Claim 7 is obvious

119. It is my opinion that each element of claim 7 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*. I believe that Claim 7, which is substantively similar to claim 3, is obvious in view of *Zhang* and *Ding* for at least the same reasons I gave above for claim 3.

7. Claim 9 is obvious

120. It is my opinion that each element of claim 9 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Zhang* in view of *Ding*.

a) [9] *Zhang* discloses “The multi-layered wiring structure as set forth in claim 5, further comprising a copper film formed on said first film”

121. It is my opinion that *Zhang* teaches this claim element. *Zhang* discloses that the multi-layered wiring structure further includes a copper film. Ex. 1004, Abstract (disclosing that the second conductive film 54 and 64 “includes mostly copper”); 4:20-23 (“After the copper seed film 54 has been deposited, an electroplated copper film 64 is then formed over all the substrate as shown in FIG. 6.”). According to *Zhang*, the copper seed film 54 and copper film 64 may be replaced by a single copper film. *Id.*, 5:35-38. *Zhang* further discloses that the copper film 54 and 64 is formed on the first film portion 32 as recited in claim 9. *Id.*, FIG. 8 (showing copper film 54 and 64 formed on the top film 32).

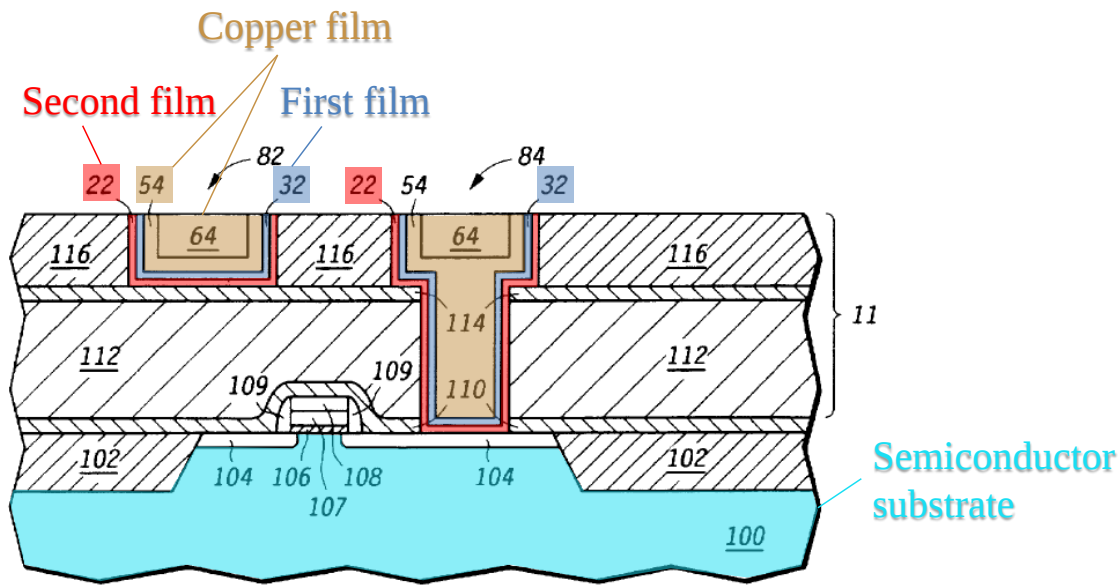
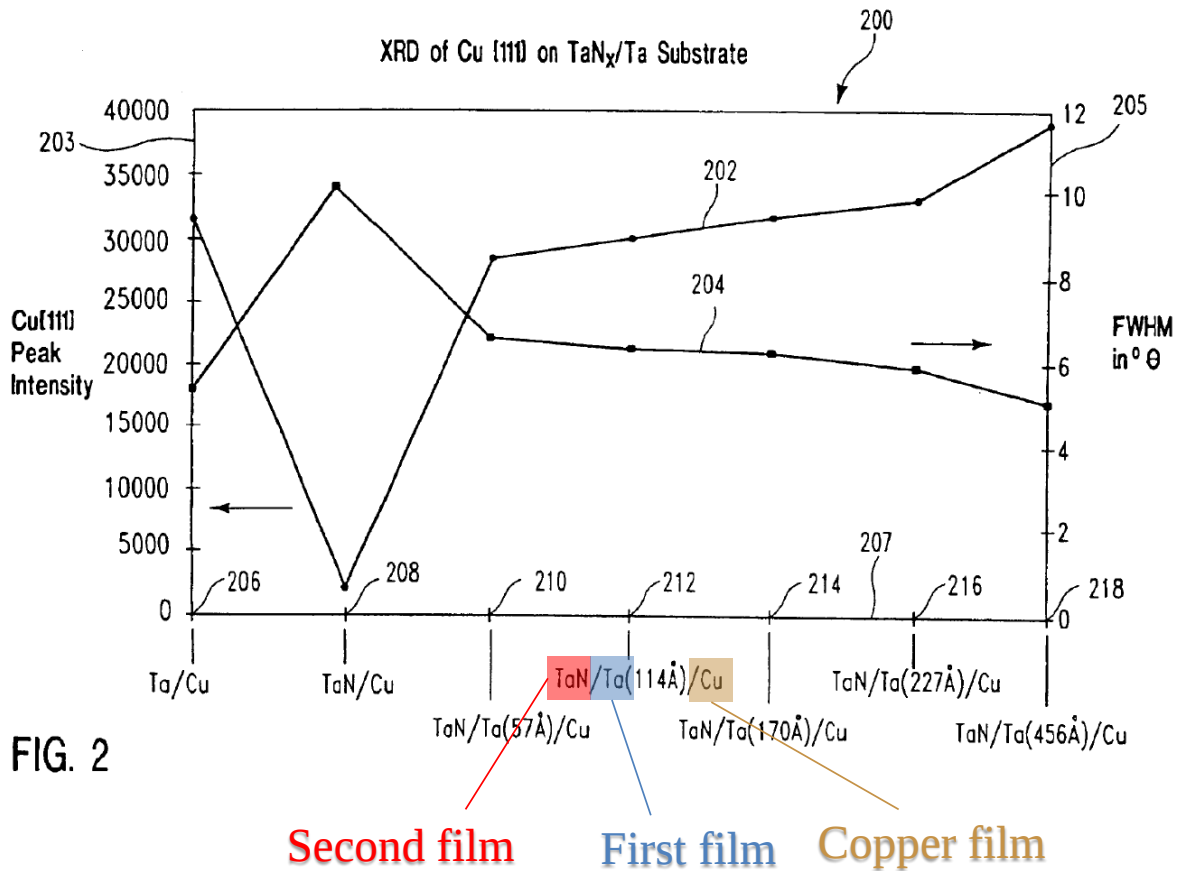


FIG. 8

Annotated FIG. 8 of *Zhang*

122. *Ding* similarly discloses a copper film formed on the first film (top film) in its two-layer diffusion barrier. See, e.g., Ex. 1005, 8:1-4 (disclosing “a tantalum <002> crystalline orientation which enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystal orientation”), FIG. 2 (“TaN/Ta(114Å)/Cu”).



Annotated FIG. 2 of Ding

C. I believe that the combined teachings of Zhang, Ding, and Sun render claims 1-3, 5-7, and 9 obvious

123. It is my opinion that each element of claims 1-3, 5-7, and 9 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of Zhang and Ding (as discussed above) and further in view of Sun. As I explained in detail above, Zhang in view of Ding renders obvious each of claims 1-3, 5-7, and 9 in the '324 patent. For claim elements [1.2] and [5.3] ("said second film being composed of amorphous metal nitride"), Zhang discloses that its second film, portion 22, is a metal (tantalum) nitride film (*id.*, 3:9

and FIG. 4) but does not explicitly disclose whether this film is amorphous. While *Ding* teaches the desirability of using an amorphous tantalum nitride (TaN_x) layer as a diffusion barrier (Ex. 1005, 3:39-41), *Sun* provides further detail.

124. Specifically, *Sun* discloses that “nitrogen can [] promote the formation of amorphous metallic alloys with most early transition metals.” Ex. 1007, 9. *Sun* also teaches that an amorphous film is a better barrier than a crystalline film because the amorphous film is “absen[t] of fast diffusion paths.” *Id.* Therefore, a POSITA would have been motivated to modify bottom portion 22 of the diffusion barrier in *Zhang* to be an amorphous tantalum nitride film (tantalum is an early transition metal), even if it is not already known to be amorphous, to avoid fast diffusion paths along grain boundaries and minimize copper diffusion. I believe that this is especially obvious because the function of portion 22 of *Zhang* is to prevent the diffusion of copper (Ex. 1004, Abstract, and 2:37-39), and this function may be improved by using an amorphous tantalum nitride film as taught by *Sun*.

125. Moreover, in my opinion, a modification of *Zhang* and *Ding* in view of *Sun* would have been obvious to a POSITA because *Zhang*, *Ding*, and *Sun* are all directed to improving diffusion barrier films in semiconductor devices with copper interconnects. See, e.g., Ex. 1004, 2:38-39; Ex. 1005, 3:33-38; Ex. 1007 at 9 (“In the recent past tantalum nitride has attracted attention . . . as a thin film diffusion barrier between silicon and. . . Cu”). Further, I believe that the proposed

modification would have been obvious because both *Zhang* and *Ding* address problems of using tantalum nitride as a diffusion barrier with copper films, and *Sun* investigates how various nitrogen concentrations in TaN_x affect its diffusion barrier properties. *See, e.g.*, Ex. 1004, 1:33-34 (“tantalum nitride has adhesion problems with some types of copper films”); Ex. 1005, 3:28-32 (“copper deposited directly over TaN_x does not exhibit a sufficiently high degree of $\langle 111 \rangle$ crystal orientation to provide the desired copper electromigration characteristics.”); Ex. 1007, 9 (“We deposited Ta-N films by reactive r.f. sputtering from a Ta target with an N_2 -Ar gas mixture. Alloys over a composition range 0-60 at.% N have been synthesized. We report on their composition, structure and electrical resistivity.”).

126. Moreover, in my opinion, any such modification of the layer 22 of *Zhang* in view of *Ding* and further in view of *Sun* would have used well-known, common techniques such as those expressly taught by *Zhang*, *Ding*, and *Sun*, including for example sputtering deposition of the first and second films of the diffusion barrier. *See, e.g.*, Ex. 1004, 3:48-50; Ex. 1005, 6:24-57, Ex. 1007, 9. And such straightforward modifications would have maintained the known purpose and functionalities of *Zhang* without any significant changes. *See, e.g.*, Ex. 1004, 2:38-39 (stating that layer 22 (first portion) “provides a good diffusion barrier”); Ex. 1005, Abstract (teaching that an amorphous layer “[prevents] the diffusion of copper into the underlying substrate”); Ex. 1007, 9 (teaching that an amorphous

film is a better barrier than a crystalline film because the amorphous film is “absen[t] of fast diffusion paths.”).

127. Finally, I believe that the proposed modification produces no unexpected results but instead behaves exactly as a POSITA at the time would have predicted. *See, e.g.*, Ex. 1005, Abstract (teaching that an amorphous layer “[prevents] the diffusion of copper into the underlying substrate”); Ex. 1007 (teaching that an amorphous film is a better barrier than a crystalline film because the amorphous film is “absen[t] of fast diffusion paths.”); *compare* Ex. 1001, 3:16-19, 3:22-27 (teaching that “amorphous TaN . . . does not have the paths through which copper is diffused unlike the crystalline metal film” and thus “would have high barrier characteristic of preventing copper diffusion.”).

D. I believe that the combined teachings of *Ding* in view of *Zhang* render claims 1-3, 5-7, and 9 obvious

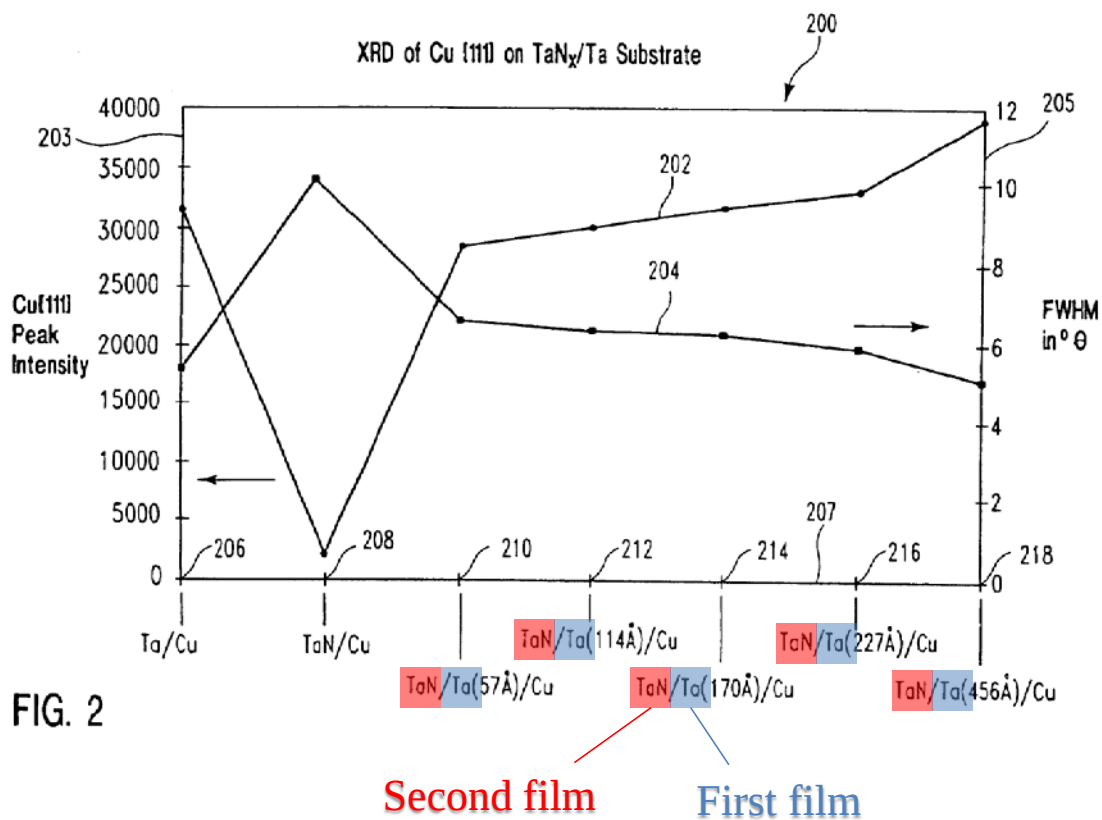
4. Claim 1 is obvious

128. It is my opinion that each element of claim 1 would have been obvious to a POSITA as of the filing date of the ’324 patent based on the combined teachings of *Ding* in view of *Zhang*.

1. [1.0] *Ding* discloses “A barrier film preventing diffusion of copper from a copper wiring layer formed on a semiconductor substrate, comprising a multi-layered structure of first and second films”

129. It is my opinion that *Ding* teaches this claim element. *Ding* discloses a barrier film (“a barrier layer structure”) preventing diffusion of copper from a

copper wiring layer. Ex. 1005, Abstract (“a barrier to the diffusion of a copper layer deposited thereover”). *Ding* discloses that the barrier film (“barrier layer structure”) is formed on a semiconductor substrate. *Id.*, 6:38 (“deposited on the surface of semiconductor workpiece 116”). *Ding* also discloses the barrier film comprises a multi-layered structure of first (“a second layer of Ta”) and second films (“a first layer of TaN_x”). *Id.*, Abstract, 4:66-67, 6:64, and FIG. 2.



Annotated FIG. 2 of *Ding*

2. [1.1] *Ding* in view of *Zhang* discloses “said first film being composed of crystalline metal containing nitrogen therein”

130. In my opinion, this claim element would have been obvious to a POSITA at the time of the '324 patent based on *Ding* in view of *Zhang*. *Ding* discloses that the first film (“second layer of Ta”) is composed of a crystalline metal (tantalum). Ex. 1005, 7:67-8:4 (teaching a tantalum layer that provides “a tantalum <002> crystalline orientation which enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystalline orientation”) (emphasis added). In *Ding*, the first and second films (Ta and TaN_x) of the diffusion barrier are deposited using standard sputtering techniques. Ex. 1005, 3:47-57 (“The TaN_x layer is preferably deposited using standard reactive ion sputtering techniques” and “[t]he Ta layer is preferably deposited using standard ion sputtering techniques”).

131. In my opinion, *Ding* teaches every element of claim 1 of the '324 patent, except it does not expressly state the top tantalum layer in the barrier contains nitrogen therein. The sputter deposition parameters described in *Ding*, however, suggest the top tantalum layer may contain a small content of nitrogen. In *Ding*, both the first and second films (Ta and TaN_x) are deposited using standard sputtering techniques. Ex. 1005, 3:47-57 (“The TaN_x layer is preferably deposited using standard reactive ion sputtering techniques” and “[t]he Ta layer is preferably

deposited using standard ion sputtering techniques”). *Ding* discloses the formation of the bottom TaN_x layer by feeding both argon and nitrogen gases into a vacuum chamber. *Id.*, 7:1-12. *Ding* discloses an operational pressure in the vacuum chamber of about 1.7 milliTorr (mT) when depositing this tantalum nitride layer. *Id.*, 7:17-20. *Ding* further teaches, “Subsequent to application of the TaN layer, the nitrogen gas was shut off, “the argon gas feed was maintained,” and the “pressure in the vacuum chamber remained at about 1.7 mT” for depositing the top tantalum layer in the diffusion barrier. *Id.*, 7:21-29.

132. In my opinion, because the argon gas feed was “maintained” when the nitrogen gas was turned off, and the sputtering chamber “remained” at the same operational pressure when sputter depositing the top and bottom films, I believe that a POSITA would have understood the bottom TaN_x layer and top Ta layer in *Ding* would be fabricated using a single evacuation cycle of the vacuum chamber. In my opinion, the POSITA would also have understood that at least some residual nitrogen from depositing the TaN_x layer would remain in the sputtering chamber shown in FIG. 1 after the nitrogen gas is turned off (and during at least part of the deposition of the top tantalum layer), resulting in some nitrogen being deposited in the top tantalum layer (as required in claim element [1.1]). The POSITA would have understood the top tantalum film would contain decreasing nitrogen content as the residual nitrogen is pumped out of the chamber or deposited in the top Ta

layer after the nitrogen gas feed was turned off (following the sputter deposition of the bottom TaN_x layer).

133. Like *Ding*, *Zhang* discloses that “deposition of the two films 22 and 32 [in the diffusion barrier] is typically performed as one sequence during a single evacuation cycle.” Ex. 1004, 3:37-38. “During the first portion of the deposition [i.e., film 22] . . . a nitrogen-containing gas and an inert gas, such as argon, are directed toward a sputtering target” (*id.*, 3:41-43), and “[i]n forming film 32, the nitrogen-containing gas is terminated while the inert gas continues to flow” (*id.*, 3:44-47).

134. I understand that *Ding* used a similar sputter-deposition process as *Zhang*, but did not analyze the composition of the top Ta layer. *Zhang*, however, did the analysis and the result is shown in FIG. 4. Ex. 1004, FIG. 4. *Zhang* discovered that the content of nitrogen (in atomic percent) in the top tantalum-rich layer 32 decreases as a function of distance after the nitrogen gas has been turned off and the layer 32 continues to be deposited. *Id.*, FIG. 4. In my opinion, a POSITA at the time when the '324 patent was filed would have understood that the same decrease in nitrogen content would exist within the top tantalum layer of *Ding*, which is formed using a similar sputtering process using a single evacuation cycle.

135. I believe *Ding* does not teach against the above-discussed obvious result of having nitrogen in the top Ta layer. Although *Ding* mentions “a pure Ta barrier layer,” “a layer of pure Ta,” or a “pure layer of Ta” (*see, e.g.*, Ex. 1005, 4:11, 9:47, 10:3, 10:8), *Ding* only uses the term “pure” to distinguish a diffusion barrier having only a single layer of tantalum (i.e., a barrier that is purely tantalum) from a multi-layer barrier comprising a tantalum nitride layer and a tantalum layer. *See, e.g.*, Ex. 1005, 9:47-49 (“a layer of pure Ta does not provide a diffusion barrier which performs as well as the TaN_x/Ta barrier layer structure”), 4:6-11 (describing the Cu <111> crystallographic content of copper formed on the multi-layer TaN_x/Ta diffusion barrier as 70% of the content formed over a “pure Ta barrier layer”), 10:1-3 (with reference to FIG. 2, “[a]t data point 214 on curve 202, which represents the 500 Å TaN / 170 Å Ta barrier layer, the area under the Cu <111> [] peak is equivalent to the pure layer of Ta,” shown at data point 206 where the barrier is only Ta).

136. I note that, while *Ding* refers to a single-layer barrier made only of Ta as a “pure Ta barrier layer,” *Ding* does not use the term “pure” to describe the top Ta film in a multi-layer TaN_x/Ta barrier. In my opinion, *Ding* does not require the top tantalum film in the multi-layer TaN_x/Ta barrier to have no impurities or other components, such as nitrogen. I believe that a POSITA would have understood the top Ta layer in the multi-layer TaN_x/Ta barrier of *Ding* would contain some

nitrogen content as a result of the sputter-deposition process in view of *Zhang*'s teachings.

137. I was informed that the Patent Owner may argue that *Ding* requires the top Ta layer in the TaN_x/Ta diffusion barrier to contain no nitrogen content. I do not agree, for reasons explained in the preceding paragraphs. Notwithstanding, a POSITA at the time of the '324 patent's filing date would have been motivated to modify the teachings of *Ding* to incorporate a small amount of nitrogen into *Ding*'s top Ta layer in view of the process disclosed by *Zhang*, thereby rendering obvious the claimed "first film being composed of crystalline metal containing nitrogen therein."

138. I believe that it would have been obvious for a POSITA at the time of the '324 patent's filing date to modify the top Ta layer of the two-layer barrier of *Ding* to contain nitrogen in view of *Zhang* for at least the following reasons.

139. In my opinion, a POSITA at the time of the application leading to the '324 patent would have been motivated to incorporate nitrogen into the top Ta film of the diffusion barrier in *Ding* because doing so would provide several predictable technical benefits compared with using a tantalum film without any nitrogen. The POSITA would have understood that adding nitrogen to *Ding*'s tantalum film would provide well-known benefits to the diffusion barrier, including better polishing characteristics (*see, e.g.*, Ex. 1019, at 12-13, Table 1; Ex. 1021, Table I),

lower resistivity (*see, e.g.*, Ex. 1015, Table 1), and more effective blocking of copper diffusion for *Ding*'s diffusion-barrier structure (*see, e.g.*, Ex. 1023, at 8). As explained above, the POSITA would have used the single-evacuation cycle sputtering process taught by *Zhang* to incorporate a small amount of nitrogen into the top tantalum film in *Ding*.

140. In my opinion, a POSITA would have been motivated to incorporate nitrogen into the top, tantalum layer of *Ding* because of the features of the diffusion barrier in *Zhang*. *Zhang*, for example, teaches the removal of the barrier films 22 and 23 using CMP. FIGS. 7 and 8 (removal of barrier films 32 and 22 using a polishing process), 4:34-37 (same). *Ding* similarly teaches CMP to remove its top and bottom barrier films. Ex. 1005, 7:56-59.

141. *Zhang* teaches that although "a pure tantalum film or a tantalum nitride film is used as a barrier/adhesion film for a copper interconnect," the tantalum film "can be very difficult to remove using a polishing process." Ex. 1004, 1:30-34; FIGS. 7 and 8 (removal of barrier films 32 and 22 using a polishing process), 4:34-37 (same). The difficulty in removing the tantalum film may cause "the copper . . . be over polished, creating a 'dishing effect' in the area of a contact" and "there is a cost in substrate processing time." Ex. 1005, 7:61-65.

142. In my opinion, a POSITA would have appreciated that incorporating a small amount of nitrogen into the top tantalum layer in *Ding*, as taught in *Zhang*

(e.g., Ex. 1004, FIG. 4), may have had the advantage of making the top tantalum film in *Ding* more easily removable using a chemical mechanical polishing process. See, Moussavi et al., “Comparison of Barrier Materials and Deposition Processes for Copper Integration,” Proceedings of the IEEE 1998 International Interconnect Technology Conference, pp. 295-97 (1998) (“Moussavi,” Ex. 1019), at 12-13, Table 1 (showing Ta has a higher polishing selectivity against Cu than TaN, which means the polishing rate of Ta is lower than that of TaN); Wijekoon et al., “Development of a Production Worthy Copper CMP Process,” 1998 IEEE/SEMI Advanced Semiconductor Manufacturing Conference, pp. 354-63 (1998) (“Wijekoon,” Ex. 1021), Table I).

143. I believe that the POSITA would have appreciated that incorporating a small amount of nitrogen into the top tantalum layer in *Ding*, as taught in Zhang (e.g., Ex. 1004, FIG. 4) might have the advantage of making the top tantalum film in *Ding* more easily removable using a polishing process, thus minimizing the “dishing effect” and saving processing time and cost. See Ex. 1005, 7:61-65.

144. In my opinion, it was also well known to a POSITA at the time of the ’324 patent that tantalum without any impurities (such as nitrogen) has inferior diffusion barrier characteristics because grain boundaries in the tantalum act as fast diffusion paths that would promote rather than inhibit copper diffusion. See Ex.

1007, 9 (“amorphous . . . metal nitrides . . . [is] absent[t] of fast diffusion paths as they exist in polycrystalline films”).

145. I believe that POSITA at the time of the '324 patent would have known that even adding a small amount of nitrogen to a tantalum thin film would allow the nitrogen to segregate to the grain boundaries and block the fast diffusion paths along those boundaries. See Wang et al., “Barrier Properties of Very Thin Ta and TaN layers Against Copper Diffusion,” J. Electrochem. Soc., Vol. 145, No. 7, pp. 2538-45 (“Wang”, Ex. 1023), at 8 (“[t]he barrier properties of Ta can be significantly improved by adding impurities, such as N and O, to the Ta film. If solubility limit of the impurity is exceeded, solute atoms in the Ta grain are expected to be segregated to the grain boundaries, resulting in obstruction of the fast paths for copper diffusion”). Although one purpose of the top tantalum layer in *Ding* is to provide good adhesion with an overlying copper layer, I believe the POSITA would have appreciated that increasing the diffusion barrier characteristics of *Ding*’s top tantalum layer (without significantly degrading the adhesion/wetting to copper) would be beneficial for increasing the overall diffusion-barrier performance of the barrier.

146. In my opinion, the POSITA would have been motivated to modify the sputter-deposition process of *Ding* according to the teachings of *Zhang*, to add a small amount of nitrogen into *Ding*’s top tantalum layer, because doing so would

add interstitial nitrogen along the tantalum grain boundaries to improve the overall performance of the TaN_x/Ta diffusion barrier.

147. To my knowledge, it was also well known to a POSITA at the time of the '324 patent that maintaining a low resistance in the copper metal wiring layer and adhesion layer/diffusion barrier was desirable to reduce the device's power consumption and RC delays (which are both directly proportional to resistance). A POSITA would also have recognized that it was known that adding a small amount of nitrogen to a tantalum layer would reduce the resistivity of that layer. Ex. 1015, Stavrev at Table 1, showing the change of resistivity in a nitrogen-containing tantalum film with changing nitrogen flow during deposition (and thus changing nitrogen content), in particular showing a local minimum in resistivity in the nitrogen-containing tantalum film when some nitrogen, using a 1.5 sccm flow rate (resulting in an N/Ta ratio between 0.14 and 0.21), is added to the layer during sputter deposition. Table 1 of *Stavrev* shows the local minimum when the nitrogen flow rate is 1.5 sccm, which resulted in an N:Ta ratio between 0.14 and 0.21). I believe that a POSITA, with the desire to reduce the resistivity of the diffusion barrier, would have been motivated to modify the sputter-deposition process of *Ding* according to the teachings of *Zhang*, to add a small amount of nitrogen into *Ding*'s top tantalum layer to reduce its resistivity, for example, to minimize power consumption and RC delay of the device.

148. I believe that any modifications of the two-layer barrier film of *Ding* in view of the sputter-deposition process in *Zhang* would have used well-known, common techniques, such as similar manufacturing processes to create the top and bottom films of dual-layer diffusion barriers diffusion barriers. See, e.g., Ex. 1004, Abstract, 3:29-50 (teaching that the tantalum nitride and tantalum-rich tantalum nitride films 22 and 32 are formed using sputtering deposition); Ex. 1005, 3:28-38, 3:47-57 (“The TaN_x layer is preferably deposited using standard reactive ion sputtering techniques” and “[t]he Ta layer is preferably deposited using standard ion sputtering techniques”).

149. In my opinion, *Ding* and *Zhang* use similar sputter-deposition techniques for forming the top and bottom films. See, e.g., Ex. 1005, 6:63-7:29; Ex. 1004, 3:21-50. *Ding* discloses sputter depositing the bottom TaN_x film using a mixture of argon and nitrogen gases, then “[s]ubsequent to application of the TaN layer, the nitrogen was shut off . . . and the argon gas feed was maintained” to deposit the top tantalum film. Ex. 1005, 6:64-7:29. Similarly, in *Zhang*, the “deposition of the two films 22 and 32 is typically performed as one sequence during a single evacuation cycle” (Ex. 1004, 3:37-38), where the bottom TaN_x film 22 is sputter-deposited using a mixture of argon and nitrogen gases, then the nitrogen gas is terminated while the argon continues to maintain a plasma for sputter-depositing the top tantalum-rich tantalum nitride film 32 (*id.*, 3:41-47).

150. In my opinion, the combination of *Ding* in view of *Zhang* would have yielded predictable results to a POSITA since the sputter-deposited films in both the diffusion barriers of *Ding* and *Zhang* provide good diffusion-barrier characteristics and an improved interface between the diffusion barrier and an overlying copper wiring layer. *Ding* teaches a top crystalline film “enables easy wetting of the tantalum surface by the copper and depositing of a copper layer having a high <111> crystal orientation ...” (Ex. 1005, 8:1-4), while a bottom amorphous film “[prevents] the diffusion of copper into underlying silicon or silicon oxide surfaces” (*id.*, 3:39-41). Addressing these same diffusion and adhesion issues, *Zhang* teaches “[t]he combination of portions within the first conductive film provides a good diffusion barrier (first portion) and has good adhesion (second portion) with the second conductive film.” Ex. 1004, 2:37-40; *see also id.*, 5:49-53.

151. In my opinion, it would have been well known to a POSITA that incorporating the small amount of nitrogen into the top, second layer of Ta in *Ding* would not have prevented this top layer from being crystalline. *See, e.g.*, Ex. 1006, 9 (disclosing both a Ta film and a Ta(N) film with 5 atomic percentage nitrogen have the same crystalline phase, β -Ta: “a 0.25% N₂/Ar mixture produced a film with 5 at.% nitrogen content” and “[e]lectron-diffraction patterns taken from through-foil transmission electron microscopy (TEM) specimens allowed the

identification of β -Ta in [this] case”; “[t]he Ta film deposited in pure Ar was also found to be β -Ta.”). Further, in my opinion, the POSITA also would have known that increasing the substrate temperature or applying a biasing voltage to the substrate during the sputter deposition could help maintain the crystalline phase. See Ex. 1017, 17 (“both substrate preheating and substrate biasing during sputtering seem to have the common effect of increasing the adatom mobility and promoting a continuous, closely-packed-grains structure in the film”).

152. I believe that a POSITA also would have understood that the combination of *Ding* and *Zhang* would not produce unexpected results, but instead would behave exactly as the POSITA at the time would have predicted. See, e.g., Ex. 1005, 3:39-41, 8:1-4 (teaching that crystalline metal layer enables the “easy wetting of the tantalum surface by the copper[, i.e., good adhesion to the copper layer,] and depositing of a copper layer having a high $\langle 111 \rangle$ crystal orientation,” i.e., providing good adhesion to the copper layer, while an amorphous layer “[prevents] the diffusion of copper into the underlying substrate”); see also Ex. 1001 (teaching a copper film formed on a crystalline metal film “would have high adhesion and rich crystal orientation” but poor “barrier characteristic of preventing copper diffusion” while “amorphous TaN . . . does not have the paths through which copper is diffused unlike the crystalline metal film” and thus “would have high barrier characteristic of preventing copper diffusion”).

3. [1.2] *Ding* discloses “said second film being composed of amorphous metal nitride”

153. It is my opinion that *Ding* teaches this claim element. *Ding* discloses the second film of the diffusion barrier (which *Ding* refers to as the first layer of TaN_x) is a tantalum nitride layer, which is a metal nitride. Ex. 1005, Abstract, and 6:64. Further, the TaN_x layer in *Ding* is amorphous. *Id.*, Abstract and 3:39-40 (teaching that the TaN_x layer is “sufficiently amorphous”).

4. [1.3] *Ding* discloses “said barrier film being constituted of common metal atomic species”

154. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that top film of the barrier is composed of tantalum (which *Ding* refers to as the second layer of tantalum), or a tantalum layer containing nitrogen (as modified according to *Zhang*), and the second film of the diffusion barrier is composed of tantalum nitride, TaN_x. Ex. 1005, 3:33-34 (“We have developed a barrier layer structure comprising a layer of Ta overlying a layer of TaN_x”), 4:66-5:1 (“TaN_x/Ta barrier layer structure”). As such, in my opinion, *Ding* discloses the barrier layer structure is constituted of common metal atomic species, namely, tantalum. Ex. 1005, Abstract, 4:66-67, 6:64. [1.4] *Ding* discloses “said first film being formed on said second film”

155. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that the first film (the Ta layer) is formed on the second film (the TaN_x layer). Ex. 1005, 7:1-29; *see also*, Abstract, 4:66-5:1 (“The TaN_x/Ta barrier layer structure”).

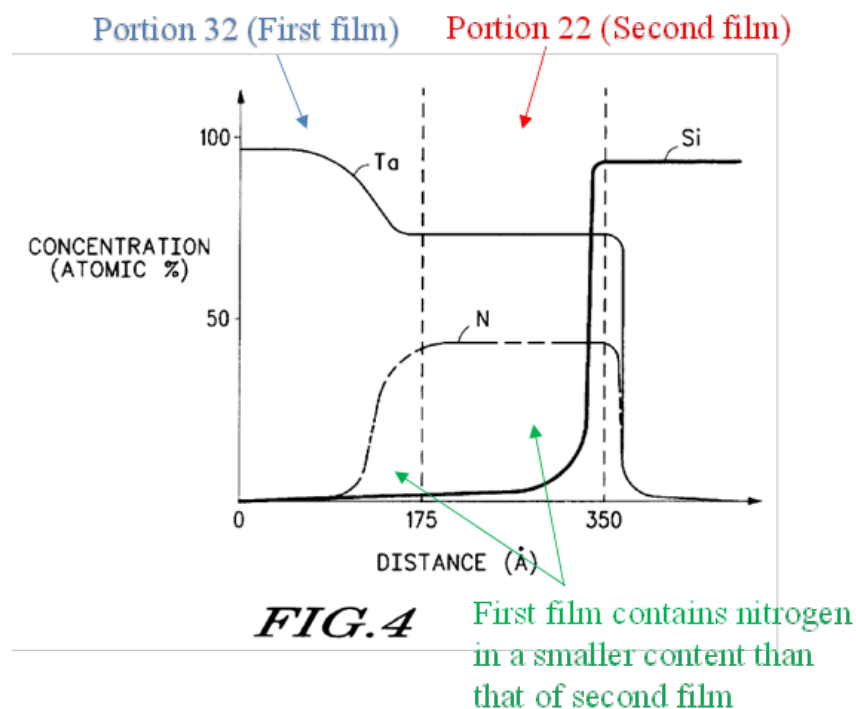
5. [1.5] *Ding* discloses “said first film in direct contact with said second film”

156. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that the Ta layer is in direct contact with the TaN_x layer. *See* Ex. 1005, 3:33-34 (“We have developed a barrier layer structure comprising a layer of Ta overlying a layer of TaN_x”), 7:21-29 (describing the formation of the second layer directly on the first layer, whereby “[s]ubsequent to application of the TaN layer, the nitrogen gas was shut off” to form the Ta layer).

6. [1.6] *Ding* in view of *Zhang* discloses “said first film containing nitrogen in a smaller content than that of said second film”

157. In my opinion, this claim element would have been obvious to a POSITA at the time of the '324 patent based on *Ding* in view of *Zhang*. In an exemplary embodiment, *Ding* discloses that “the TaN_x layer produced was TaN_{0.7}, containing about 40 atomic percent nitrogen.” *Id.*, 7:11-12. *Ding* further discloses that “[s]ubsequent to application of the TaN layer, the nitrogen gas was shut off” to deposit “a . . . layer of tantalum . . . over the TaN layer.” *Id.*, 7:21-27. In my opinion, since the nitrogen gas was shut off when forming the top tantalum layer of *Ding* in a single sputtering deposition sequence for forming the diffusion barrier,

there is less atomic percent nitrogen in the top tantalum layer than in the bottom tantalum nitride layer. As I explained in detail above, I believe that a POSITA would have been motivated to incorporate a small amount of nitrogen into the second layer of tantalum in *Ding* by using a sputter-deposition process similar to that disclosed by *Zhang*. As shown in the plot of FIG. 4 in *Zhang*, such a process would result in a smaller content of nitrogen in the barrier's first film (second layer of Ta, as modified to contain nitrogen by the process of *Zhang*) than in its bottom film (first layer of TaN_x) in *Ding*.



Annotated FIG. 4 of *Zhang*

5. Claim 2 is obvious

158. It is my opinion that each element of claim 2 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*.

1. [2] *Ding* discloses “The barrier film as set forth in claim 1, wherein said second film has a thickness in the range of 80 Angstroms to 150 Angstroms both inclusive”

159. *Ding* discloses embodiments where the second film (bottom TaN_x film) of the diffusion barrier has a thickness “ranging from greater than about 10 Å to about 300 Å,” which contains the claimed range of 80 Å to 150 Å in claim 2. Ex. 1005, Abstract. As such, *Ding* discloses the thickness range of claim 2 for the bottom TaN_x film.

160. In my opinion, *Ding*’s disclosed range of “greater than about 10 Å to about 300 Å” teaches the claimed range of 80 to 150 Angstroms with sufficient specificity because the claimed range falls completely within *Ding*’s disclosed range, and the disclosed 10 to 300 Angstroms in *Ding* is a small subset of a larger range of 50 to 1000 Angstroms disclosed in *Ding* for the same layer. Ex. 1005, 4:14-15.

161. I understand that the only reason the '324 patent provides for having a second-film thickness in the range from 80 to 150 Angstroms is so that “barrier characteristic of preventing copper diffusion is ensured and adhesion with the

underlying insulating film . . . is also ensured” (Ex. 1001, 13:51-54), but the patent provides no evidence that using a film with a thickness in either of the ranges 10 to 80 Angstroms or 150 to 300 Angstroms would fail to prevent copper diffusion or proper adhesion with the underlying insulating film. In my opinion, the POSITA would have been able to choose an appropriate second film thickness in the claimed range, for example, based on the desired diffusion blocking, adhesion, resistivity, and amorphization properties of the diffusion barrier.

162. In general, I believe that it was well known to a POSITA that for the same degree of amorphization (which is determined by N content and sputtering conditions), a thicker film would lead to better diffusion barrier properties. In my opinion, a POSITA would also have understood that a thicker film would also lead to a lower electrical resistance in a copper/barrier structure along a direction parallel to the interface between the barrier and the copper layer and a higher electrical resistance along a direction perpendicular to the interface. Moreover, it was understood that the thicker film could also lead to more stress because of the lattice mismatch and the thermal expansion mismatch between the TaN_x and the underlying dielectric, which may lead to adhesion problems. Because these concerns are well-known design criteria to a POSITA at the relevant time, I believe that the range claimed in Claim 2 would have been obvious to a POSITA at the relevant time because a POSITA would have selected an optimal thickness both

within and reasonably beyond the claimed range based on these well-known design criteria.

163. Also, how “amorphous” the TaN_x film is affects its optimum thickness. Generally, the crystallinity of solids ranges from amorphous (with no short range periodicity of the atoms in the material), to small grain microcrystalline films (with short range periodicity of the atoms within the small grains), to larger grain polycrystalline films (with longer range periodicity of the atoms within the larger grains), to single crystal or single crystalline solids (with long range periodicity over the entire solid). Generally speaking, the more amorphous the TaN_x film is, the thinner it can be in order to block diffusion. Therefore, the optimal thickness for the second film would have varied, depending on the amorphous nature of the film, and a POSITA would have understood such a thickness to be a simple design choice.

164. Moreover, where the TaN_x film is located and how it is used affects its optimum thickness. For example, if the barrier layer rests on an inter-metal dielectric (IMD) rather than on a typical Si substrate, a POSITA would have understood that a thinner TaN_x barrier layer is permissible (perhaps down to 10 Angstroms for the vias), because the IMD layers are relatively far away from the Si surface. On the other hand, a POSITA would have understood that a barrier layer on the contacts to a Si substrate may be required to be designed to be thicker (with

a lower limit of 50 Angstroms in *Ding*) as added insurance such that Cu does not enter Si. Copper diffusing into Si is the real problem in terms of decreasing minority carrier lifetimes and degrading device performance, while Cu atoms diffusing into the IMDs above are only problematic in the sense that the Cu could ultimately find its way into the Si underneath. Therefore, the optimal thickness for the second film would have varied depending on where the film is located in the structure and how it is used, and a POSITA would have understood such a thickness to be a simple design choice.

165. To the extent *Ding* does not expressly disclose the thickness range for the second film in this claim element, which corresponds to the thickness of *Ding*'s TaN_x film (Ex. 1005, 4:14), I believe that the claimed thickness range would have been obvious to a POSITA, in view of the thickness of the bottom TaN_x film in *Zhang*. Ex. 1004, 3:9-12 ("tantalum nitride film 22 is then deposited"). *Zhang* teaches a "typical" combined thickness of the top and bottom films 32 and 22 in the range of 100 to 300 Angstroms (Ex. 1004, 4:7-10), and also teaches an embodiment where the thickness of the films 32 and 22 may be approximately equal (Ex. 1004, 4:1-5, FIG. 4,), therefore disclosing a thickness range for film 22 in the range of 50 to 150 Angstroms (i.e., half of the disclosed range of 100 to 300 Angstroms for the combined thickness of films 32 and 22). This range includes the claimed range of 80 to 150 Angstroms with sufficient specificity because the

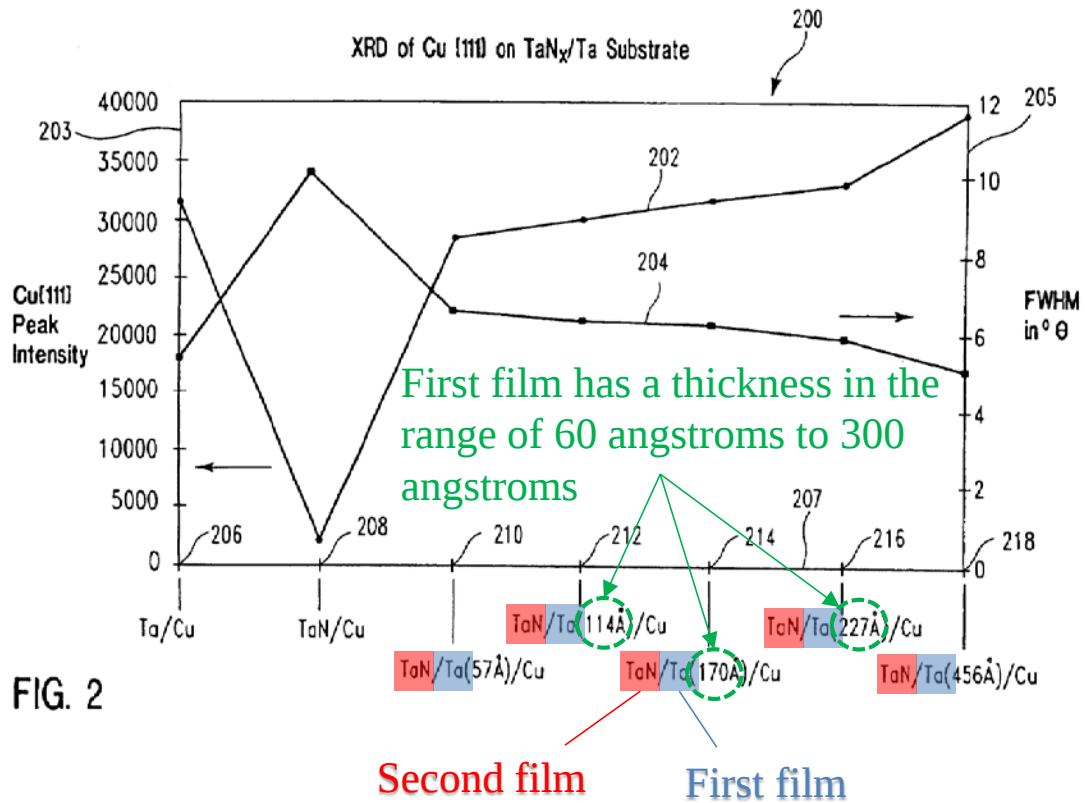
ranges overlap for the most part, from 80 to 150 Angstroms, with the only non-lapping range from 50 to 80 Angstroms representing a small percentage of the overall range. In my opinion, a POSITA would have been motivated to combine the teachings of *Ding* with *Zhang* for at least the same reasons I gave above.

6. Claim 3 is obvious

166. It is my opinion that each element of claim 3 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*.

1. [3] *Ding* discloses “The barrier film as set forth in claim 1, wherein said first film has a thickness in the range of 60 Angstroms to 300 Angstroms both inclusive”

167. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that the first film (the Ta layer) has a thickness “ranging from about 5 Å to about 500 Å, wherein the thickness is preferably greater than about 20 Å” (Ex. 1005, 3:52-55), which includes the claimed range of 60 Angstroms to 300 Angstroms. *Ding* discloses specific embodiments where the thickness of the top tantalum film is 114 Å, 170 Å, and 227 Å, each of which falls within the range of first-film thickness in claim 3. *Id.*, 8:66-9:4 (“the overlying Ta layer was 114 Å thick”; “the overlying Ta layer was 170 Å thick”; “the overlying Ta layer was 227 Å thick”), FIG. 2.



Annotated FIG. 2 of *Ding*

7. Claim 5 is obvious

168. It is my opinion that each element of claim 5 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*.

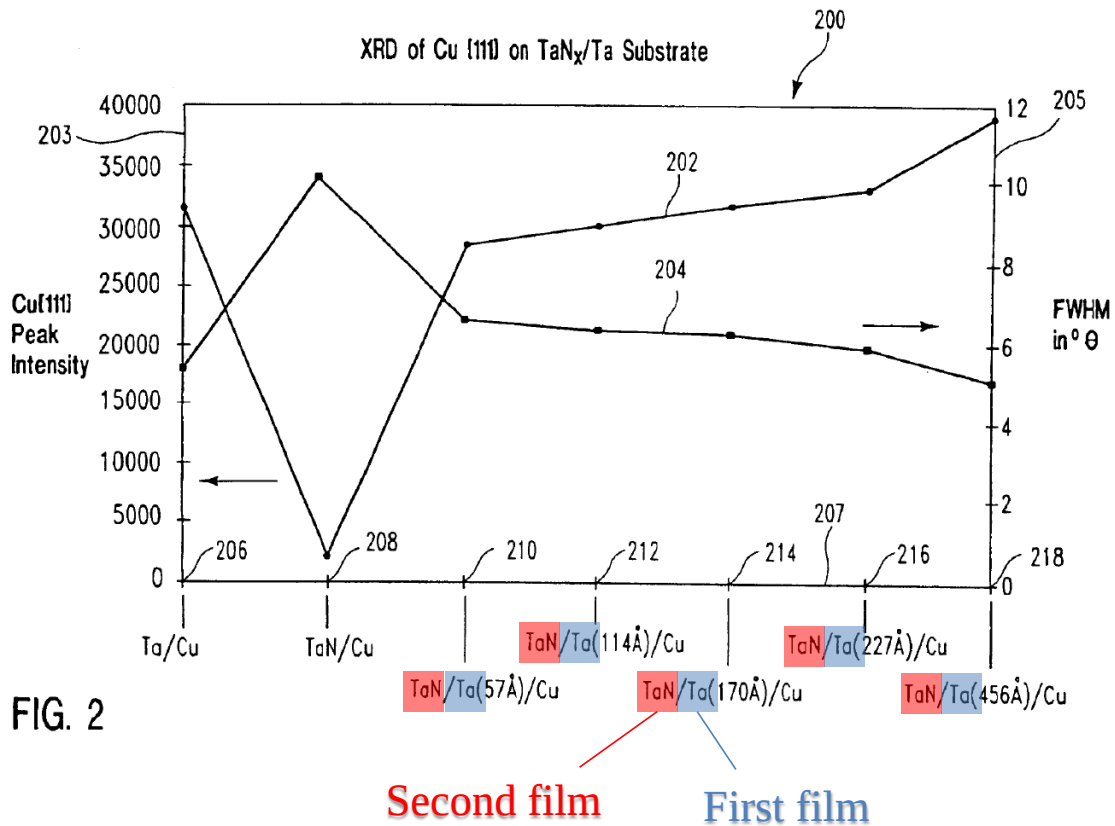
1. [5.0] *Ding* discloses “A multi-layered wiring structure comprising a barrier film which prevents diffusion of copper from a copper wiring layer formed on a semiconductor substrate”

169. It is my opinion that *Ding* teaches this claim element. I understand that claim 5 differs from claim 1 only in that claim 5 claims a multi-layered wiring structure comprising the barrier film of claim 1. As I explained above, *Ding*

teaches a multi-layered wiring structure comprising a barrier film (*see, e.g.*, Ex. 1005, 4:5-7 “a copper interconnect structure comprising a copper layer deposited over a barrier layer structure”) which provides “a barrier to the diffusion of a copper layer deposited thereover.” *Id.*, Abstract. *Ding* discloses that the barrier film is formed on a semiconductor substrate. *Id.*, 6:38 (teaching the barrier layer structure is “deposited on the surface of semiconductor workpiece 116,” which is a semiconductor substrate).

2. [5.1] *Ding* discloses “said barrier film having a multi-layered structure of first and second films”

170. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that the barrier film has a multi-layered structure of first and second films, which respectively correspond to the second layer of tantalum (or tantalum containing nitrogen as modified by *Zhang*) and the first layer of TaN_x in *Ding*. Ex. 1005, Abstract, 4:66-67, 6:64, and FIG. 2.



Annotated FIG. 2 of *Ding*

3. *Ding* and *Zhang* disclose [5.2]-[5.7]

171. Claim elements [5.2]-[5.7] of claim 5, which are substantively similar to the elements [1.1]-[1.6] of claim 1, are obvious over *Ding* in view of *Zhang* for at least the same reasons explained above for claim elements [1.1]-[1.6].

8. Claim 6 is obvious

172. It is my opinion that each element of claim 6 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*. Claim 6, which is substantively similar to

claim 2, is obvious over *Ding* in view of *Zhang* for at least the same reasons explained above for claim 2.

9. Claim 7 is obvious

173. It is my opinion that each element of claim 7 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*. Claim 7, which is substantively similar to claim 3, is obvious over *Ding* in view of *Zhang* for at least the same reasons explained above for claim 3.

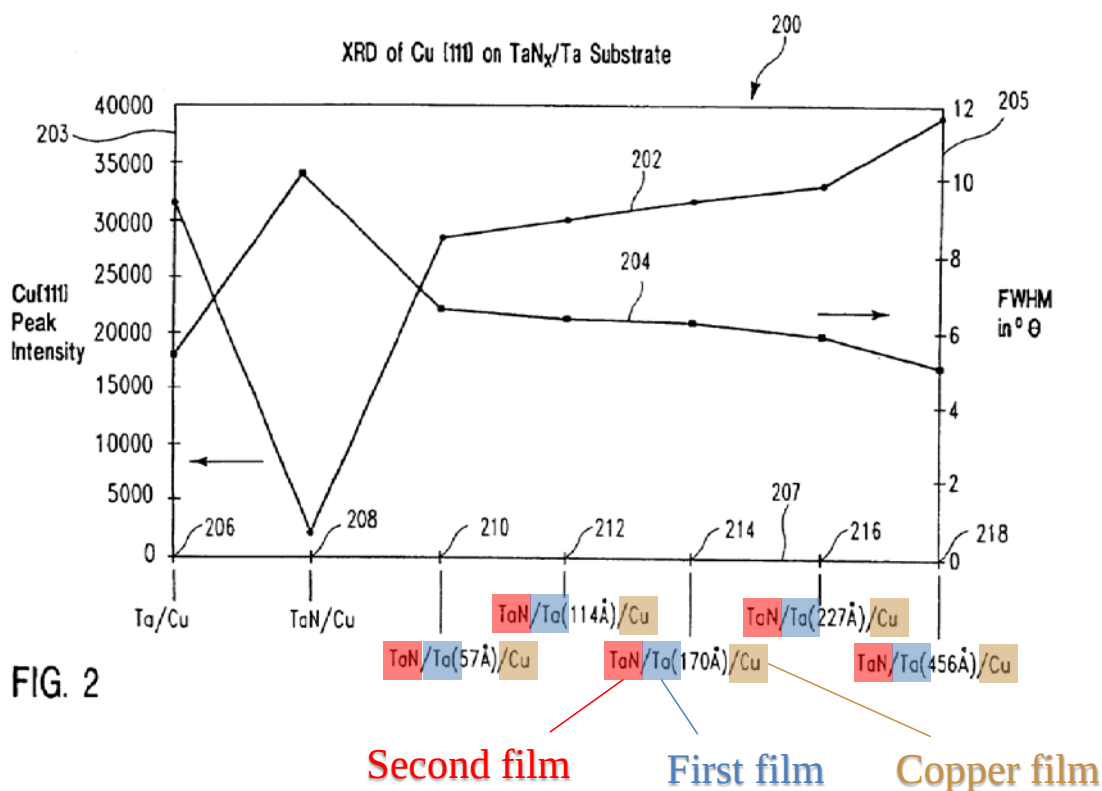
10. Claim 9 is obvious

174. It is my opinion that each element of claim 9 would have been obvious to a POSITA as of the filing date of the '324 patent based on the combined teachings of *Ding* in view of *Zhang*.

1. [9] *Ding* discloses “The multi-layered wiring structure as set forth in claim 5, further comprising a copper film formed on said first film”

175. It is my opinion that *Ding* teaches this claim element. *Ding* discloses that the multi-layered wiring structure (“copper interconnect structure”) further includes a copper film (copper layer) formed on the first film (the Ta layer) in the diffusion barrier. See, e.g., *id.*, 4:5-7, 4:14-24, 4:66, 7:38-50 (teaching how the copper layer is deposited and, in particular, that the “copper layer overlying the TaN barrier layer was applied,” where the substrate for depositing the copper layer is a “substrate[] having a tantalum layer as its upper surface”), 8:2-3 (“[t]he

[tantalum] layer . . . enables easy wetting of the tantalum surface by the copper,” which, in my opinion, means the copper layer contacts the tantalum layer), and FIG. 2.



Annotated FIG. 2 of *Ding*

Conclusion

176. In signing this declaration, I recognize that the declaration will be filed as evidence in a contested proceeding before the Patent Trial and Appeal Board of the United States Patent and Trademark Office. I also recognize that I may be subject to cross-examination in the proceeding and that cross-examination will take place within the United States. If cross-examination is required of me, I

will appear for cross-examination within the United States during the time allotted for cross-examination.

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

Dated: June 24, 2016

By: 
Sanjay Kumar Banerjee

Attachments:

Appendix A: Curriculum Vitae of Sanjay Kumar Banerjee

Appendix A

Dr. Sanjay Banerjee
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CV at http://www.mrc.utexas.edu/people/faculty/sanjay-banerjee

Selected Testifying Experience (**represented the underlined party in each case**)

1. Freescale vs. Marvell (Case No. 12-CV-644 in W.D. Texas; **deposed**), DRAM, Brian Mack, Quinn Emanuel, 2014
2. Cypress vs. GSI (3:13-CV-02013-JST in Northern District of CA, **expert report, deposed**, settled), Semiconductor Memory architecture, Brent Yamashita, DLA Piper, 2014
3. Crocus vs. NYU (Case IPR2014-00047 Patent 6,980,469 B2, **deposed**), STTRAM, Stephanie Schoenwald, Steptoe & Johnson, 2014
4. HSM vs. Qualcomm (Case 1:11-CV-00770-RGA in Delaware), settled, Memory sense amps, Drew Koning, Cooley, 2014, settled.
5. Spancion vs. Macronix (ITC 337-TA-893, **testified at ITC**), settled, Flash memory, Janice Jabido, Ropes and Gray, 2014
6. TPL vs. Seiko, Dell, HP, Acer, Newegg, Brother (ITC Investigation No. 337-TA-841; **testified at ITC** on behalf of all 6 respondents and won), Flash memory, Matt Hertko, Kirkland Ellis, Hogan Lovells, Kenyon, Banner Witkoff, Webb, 2013
7. Intellectual Ventures vs. Hynix (C.A. No. 10-1066 (SLR) (MPT), District of Delaware, Non-testifying expert), DRAMs, Brian Mack, Quinn Emanuel 2012
8. Smart Modular vs. Netlist (Case No. 2:12-CV-02319-MCE-EFB in Eastern District of California, **deposed**), Memory modules, Ed Sikorski, DLA, 2012.
9. Microsoft vs. Motorola (**deposed in ITC case 337-TA-744 and won**) Flash memory file systems, Brian Mack, Quinn Emanuel, 2011
10. Rambus vs. Samsung (Case C 05-00334 RMW; **testified in Northern District of California and won**), RDRAM, Jennifer Polse, Munger Tolles, 2008
11. Fujitsu Limited & Fujitsu Microelectronics America, Inc. vs. Nanya Technology Corporation, settled, DRAM, Shore Chan Bragalone, 2007
12. Toshiba America vs. Hynix Semiconductor, settled, DRAM, Townsend & Townsend & Crew 2005
13. Sandisk vs. STMicroelectronics, Case 337-TA-526, **Testified at ITC**, lost, Flash memory, Wilson Sonsini, 2004
14. Motorola vs. STMicroelectronics, ICs, Settled, Jones Day, 2004
15. Varian vs. Nissin (Case No.: 04-CA-375 (LY), Western District of Texas); **Deposed**; Ion implanter, settled before trial, Shearson Lehman, 2004

Sanjay Banerjee is the Cockrell Family Regents Chair Professor of Electrical and Computer Engineering and Director, Microelectronics Research Center, at the University of Texas at Austin. He is also the Director of the South West Academy of Nanoelectronics, one of three centers in the US to develop a replacement for MOSFETs. He received his B.Tech from the Indian Institute of Technology, Kharagpur, and his M.S. and Ph.D. from the University of Illinois at Urbana-Champaign in 1979, 1981 and 1983 respectively, all in electrical engineering. As a Member of the Technical Staff, Corporate Research, Development and Engineering of Texas Instruments Incorporated from 1983-1987, he worked on polysilicon transistors and dynamic random access trench memory cells used by Texas Instruments in the world's first 4Megabit DRAM. He has been Assistant Professor (1987-90), Associate Professor (1990-93), and Professor (1993-) at The University of Texas at Austin. He has over 1000 archival refereed publications/talks, 10 books/chapters, and 30 U.S. patents, and has supervised over 60 Ph.D. and 70 MS students. His students have received 10 Best Papers Awards at various conferences, and he has presented over 100 invited talks. He 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). He has won 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 in 1988, and several SRC Inventor Recognition and Best Paper Awards. He was a Distinguished Lecturer for IEEE Electron Devices Society, and the General Chair of the IEEE Device Research Conference, 2002. He is a Fellow of IEEE, APS and AAAS. He is active in the areas of beyond-CMOS nanoelectronic transistors based on 2D materials and spintronics, fabrication and modeling of advanced MOSFETs, and solar cells.

Sanjay Kumar Banerjee

Current Position: Cockrell Family Regents Chair in
Electrical and Computer Engineering, 1999-
Director, Microelectronics Research Center, 1999-

Education: University of Illinois, PhD (Electrical Engineering), 1983
University of Illinois, MS (Electrical Engineering), 1981
Indian Institute of Technology at Kharagpur, India, B. Tech (Electronics), 1979

Professional Engineer: Texas

Previous Positions: Cullen Trust Endowed Professorship in Engineering No.1, 1997-2001
University of Texas, Associate Director, Microelectronics Research Center, 1996-99
University of Texas, Professor, September 1993-
University of Texas, Associate Professor, September 1990- August 1993
University of Texas, Assistant Professor, September 1987- August, 1990
Texas Instruments, Corporate R& D, Member of Technical Staff, 1983-August 1987

Honors and Awards:

IEEE Andrew Grove Award (2014)
Fellow of American Association for Advancement of Science (2007)
Hocott Research Award, Univ. of Texas, 2007
Fellow, American Physical Society, 2006
Distinguished Alumnus Award, IIT, 2005
Industrial R&D 100 Award (with R.Singh) 2004
Electrochemical Society Thomas D. Callinan Award, 2003
Micron Professorship (2003- 10)
IEEE Millennium Medal, 2001
SRC Inventor Recognition Awards, 1994, 2000, 2009
Best Paper Awards, SRC 1998, 2006, 2009, 2010, 2014, 2015
Who's Who Listings (Marquis)
Cullen Professorship, Univ. of Texas, 1997- 2001
Distinguished Lecturer for the IEEE Electron Devices Society (1997-2003), Adcom
Member till 1998
Fellow of IEEE, 1996
Engineering Foundation Advisory Council Halliburton Award, 1991
Texas Atomic Energy Centennial Fellowship, 1990-97
NSF Presidential Young Investigator Award, 1988
Best Paper Award, IEEE International Solid State Circuits Conference, 1986
Jagadis Bose and National Science Talent Search Scholarships, India, 1974-79
Institute Medal and Swapan Saha Prize for Highest Ranking Undergraduate (ECE),
I.I.T., India, 1979
Phi Kappa Phi

Professional Society and Major Government Committees:

Technical Advisory Board: Applied Novel Devices (current) AstroWatt, DSM Semiconductors, Cambrios, Nanocoolers Inc., BeSang Memories, Organic ID and ITU Ventures; Gerson Lehmann Group, NY; Austin Community College; Asia Pacific IIIT; Rochester Institute of Technology, HSMC Foundry

IEEE Dan Noble Award Committee, 2010-13 (Chair, 2012-13)

Congressional round-table panel member on nanotechnology, Feb. 2008

Member on International Technology Roadmap for Semiconductors

Siemens Westinghouse Science Talent Contest Judge, 2003

Morgan & Claypool Publishers, Lectures in Electronic Materials & Devices, Series Editor

SISPAD, Program Committee, 2005-6

Electrochemical Society Symposium on SiGe, Program Committee, 2004

IRPS, Program Committee, 2005

12th Int. Workshop on Physics of Semiconductor Devices, Int. Advisory Committee

Int. Advisory Committee, Int. Conf. on MEMS and Nanotechnology, IIT, 2005

Program Committee, International SiGe Technology and Device Meeting, 2004-2012

IEEE Device Research Conference Technical Program Chair, 2000-01, General Chair, 2001-02

Editorial Board, Elsevier Science, 2001

IEDM Program Committee, Modeling and Simulation, Session Chair, 2001-03

ECS Session Chair, Toronto, Canada, May 2000

Program Committee, IEEE Int. Conf. Communications, Computers, Devices, Kharagpur, 2000.

IEEE Device Research Conference Program Committee/Local Arrangements Chair, 1999-2000

NSF Workshop Co-Organizer for "Front and Back-end Processes", Austin, TX 1999

Eleventh Int. Ion Implant Tech. Meet. Program Committee and Publications Chair, 1995-1996.

IEEE Symposium on VLSI Technology, Committee Member, 1992-98

NSF Workshop Organizer for "Silicon-Germanium Devices", Austin, TX 1999

IEEE University Government Industry Microelectronics Symp., General Chairman, 1994-1995

IEEE International Electron Devices Meeting, (Device Technology/ Session Chair: 1989-90)

IEEE Conf. on Electromagnetic Field Computation, Chair Comp. in Electron Dev., CA, 1992

Panel Member, SRC Conference on Integration of Novel Processes, 1991

Sponsored Research:

Grant title: "Three-Dimensional IC Technology,"

Co-Principal Investigator: S. Banerjee

Other Investigators: D.L. Kwong

Sponsoring Agency: Texas Advanced Technology Program

Duration: June 1988-August 1990.

Grant title: "High Speed Devices and VLSI Structures by Laser-Enhanced Epitaxy,"

Principal Investigator: S. Banerjee

Sponsoring Agency: Texas Advanced Technology Program

Duration: June 1988-August 1990.

Grant title: "Optoelectronic Devices by Photo-enhanced Chemical Vapor Deposition,"

Principal Investigator: S.Banerjee
Sponsoring Agency: National Science Foundation PYI
Duration: August 1988- July 1993.

Grant title: "GaAs-on-Si MESFET Modeling,"
Principal Investigator: S.Banerjee
Sponsoring Agency: Texas Instruments, Inc.
Duration: December 1988- August 1989.

Grant title: "Understanding and Modeling of Unit Processes"
Co-Investigator: S.Banerjee
Other Investigators: W.Adcock (PI), A.Tasch (Co-PI), I.Trachtenberg (Co-PI),
D.Kwong, J.Lee, T.Edgar and J.Ekerdt
Sponsoring Agency: SEMATECH and SRC
Duration: December 1988- August 1993.

Grant title: "RPCVD Epitaxial Silicon and Insulators for Use in 3-D CMOS Integrated
Circuits,"
Co-Investigator: S.Banerjee
Other Investigators: A.Tasch (P.I.), A.Cowley and R.Jones
Sponsoring Agency: Office of Naval Research
Duration: Sept. 1987- March 1990.

Grant title: "Ballistic and Quantum Transport in Si Devices at Cryogenic Temperatures"
Principal Investigator: S.Banerjee
Other Investigators: J.Lee
Sponsoring Agency: Texas Advanced Technology Program
Duration: November 1989- November 1991.

Grant title: "Polysilicon Transistor Modeling,"
Principal Investigator: S.Banerjee
Sponsoring Agency: Motorola
Duration: September, 1991-August, 1993.

Grant title: "Acquisition of High Resolution Transmission Electron Microscope,"
Principal Investigator: L.Rabenberg
Other Investigators: S.Banerjee, J.Goodenough, A.Heller, P.Ho and A.Manthiram
Sponsoring Agency: National Science Foundation
Duration: 10/92-10/93

Grant title: "Atomic Layer Epitaxy of Group IV Semiconductors,"
Co-Principal Investigator: S.Banerjee
Other Investigators: A.Tasch (P.I.), A.Cowley, J.Ekerdt and R.Jones
Sponsoring Agency: Office of Naval Research
Duration: February 1991-August 1996.

- Grant title:** "Materials and Bulk Processes"
Co-Investigator: S.Banerjee
Other Investigators: A.Tasch (PI), D.Kwong, J.Lee
Sponsoring Agency: SRC/ SEMATECH
Duration: September 1993- August 1998.
- Grant title:** "Synthesis, Growth and Analysis of Electronic Materials,"
Co-Investigator: S.Banerjee
Other Investigators: J.White (P.I) and 11 others from ECE, Chemistry and Physics
Sponsoring Agency: National Science
Duration: March 1991- March, 1996.
- Grant title:** "Transport in MOSFETs"
Principal Investigator: S.Banerjee
Sponsoring Agency: Motorola
Duration: August, 1993-August, 1994.
- Grant title:** "Flash EEPROMs"
Principal Investigator: S.Banerjee
Sponsoring Agency: AMD
Duration: May, 1993-December, 1996.
- Grant title:** "LDO Thin Film Transistors"
Principal Investigator: S.Banerjee
Sponsoring Agency: Micron
Duration: March, 1993- April, 1995.
- Grant title:** "Ultra Shallow Junction Technology"
Principal Investigator: S.Banerjee
Sponsoring Agency: SEMATECH
Duration: January 1994- December 1996.
- Grant title:** "SIMS Analysis of Polysilicon-on-Silicon"
Principal Investigator: S.Banerjee
Sponsoring Agency: SEMATECH
Duration: September 1994- August 1995.
- Grant title:** "RTP Implant Monitors"
Principal Investigator: S.Banerjee
Sponsoring Agency: SEMATECH
Duration: September 1995- August 1996.
- Grant title:** "Ultra-shallow Junction Formation and 2-D Dopant Profiling"
Principal Investigator: S.Banerjee
Other Investigators: K.Shih
Sponsoring Agency: Texas Higher Education Coordinating Board

Duration: January 1996- December 1997.

Grant title: "Analysis of Deep Submicron MOSFETs"
Principal-Investigator: S.Banerjee
Other Investigators: A.Tasch
Sponsoring Agency: Semiconductor Research Corporation
Duration: October 1998- September 1999.

Grant title: "Unrestricted Grant"
Principal Investigator: S.Banerjee
Sponsoring Agency: Various Donors
Duration: No expiration

Grant title: "Synthesis, Growth and Analysis of Electronic Materials,"
Co-Investigator: S.Banerjee
Other Investigators: J.White (P.I) and 11 others from ECE, Chemistry and Physics
Sponsoring Agency: National Science Foundation STC
Duration: March 1996- February, 2002.

Grant title: "Ultra-shallow Junction Process Integration"
Principal Investigator: S.Banerjee
Sponsoring Agency: SEMATECH
Duration: September 1997- December 2001.

Grant title: "Si and Ge Thin Film CVD, Modeling and Control"
Co-Principal Investigator: S.Banerjee
Other Investigators: J.Ekerdt (P.I.), M.Downer, I.Trachtenberg; Univ. of Wisconsin
Sponsoring Agency: Dept. of Defense-MURI
Duration: July 1995-July 2000

Grant title: "Ultra-shallow Junction Technology"
Principal Investigator: S.Banerjee
Sponsoring Agency: Texas Higher Education Coordinating Board
Duration: January 1998- August 2000.

Grant title: "Channel Engineering in Si-Ge-C MOSFETs "
Principal-Investigator: S.Banerjee
Other Investigators: A.Tasch
Sponsoring Agency: Semiconductor Research Corporation
Duration: October 1997- September 2000.

Grant title: "Advanced Annealing"
Principal Investigator: S.Banerjee
Sponsoring Agency: Texas Higher Education Coordinating Board
Duration: January 2000- December 2001.

- Grant title:** "Quantum Transport in Heterostructure MOSFETs "
Principal-Investigator: S.Banerjee
Other Investigators: A.Tasch
Sponsoring Agency: Semiconductor Research Corporation
Duration: October 1999- September 2002.
- Grant title:** "Front End Processing"
Principal-Investigator: S.Banerjee
Other Investigators: A.Tasch, D.Kwong, J.Lee
Sponsoring Agency: SRC/ SEMATECH
Duration: April 1998- March 2001.
- Grant title:** "Vertical Si-Ge-C MOSFETs "
Principal-Investigator: S.Banerjee
Sponsoring Agency: Semiconductor Research Corporation
Duration: September 2000-August 2003.
- Grant title:** "Compact Modeling of Gate Current"
Principal-Investigator: S.Banerjee
Other Investigators: F.Register
Sponsoring Agency: Semiconductor Research Corporation
Duration: July 2000- September 2003.
- Grant title:** "Ion Implantation Modeling"
Principal-Investigator: S.Banerjee
Other Investigators: A.Tasch
Sponsoring Agency: Semiconductor Research Corporation
Duration: July 2000- September 2001.
- Grant title:** "Front End Processing"
Principal-Investigator: S.Banerjee
Other Investigators: D.Kwong, J.Lee, F.Register
Sponsoring Agency: SRC/ SEMATECH
Duration: April 2001- March 2003.
- Grant title:** "MARCO Focus Center on Device Structures"
Principal-Investigator: S.Banerjee
Other Investigators: D.Kwong (with MIT, Stanford, UC Berkeley)
Sponsoring Agency: DARPA/SRC
Duration: Award announced February 2001 (3 year contract)
- Grant title:** "SiGe Flash EEPROMS with Quantum Dot Gates"
Principal Investigator: S.Banerjee
Sponsoring Agency: Texas Higher Education Coordinating Board
Duration: January 2002- December 2003.

- Grant title:** "MARCO Focus Center on Device Structures"
Principal-Investigator: S.Banerjee
Other Investigators: D.Kwong (with MIT, Stanford, UC Berkeley)
Sponsoring Agency: DARPA/SRC
Duration: Sept. 2003 (3 year contract)
- Grant title:** "High mobility Ge-channel MOSFETs "
Principal-Investigator: S.Banerjee
Sponsoring Agency: Semiconductor Research Corporation
Duration: September 2003-August 2006.
- Grant title:** "Monte Carlo and Quantum transport "
Principal-Investigator: S.Banerjee
Co-PI: L.F.Register
Sponsoring Agency: Semiconductor Research Corporation
Duration: September 2003-August 2006.
- Grant title:** "NIRT on Quantum Dot Memories "
Principal-Investigator: S.Banerjee
Other Investigators: J.Ekerdt, F.Register, G.Hwang
Sponsoring Agency: NSF
Duration: September 2003-August 2007.
- Grant title:** "High mobility Ge-channel MOSFETs "
Principal-Investigator: S.Banerjee
Sponsoring Agency: Texas Higher Education Coordinating Board
Duration: January 2004-Dec. 2005.
- Grant title:** "Advanced Materials Research Center"
Principal-Investigator: S.Banerjee
Other Investigators: 15 others
Sponsoring Agency: Texas
Duration: January 2004- Dec.2005
- Grant title:** "Advanced Processing and Prototyping Center"
Principal-Investigator: S.Banerjee
Other Investigators: 18 others
Sponsoring Agency: DARPA
Duration: 2005- Dec.2006
- Grant title:** "SiGe Nanostructures"
Co-Principal-Investigator: S.Banerjee,
Other Investigators: R.Huang
Sponsoring Agency: DOE
Duration: 2006- Dec.2009

- Grant title:** "Dopant Diffusion Modeling"
Principal-Investigator: S.Banerjee,
Other Investigators: G.Hwang
Sponsoring Agency: SRC
Duration: 2006- Dec.2009
- Grant title:** "NNIN "
Principal-Investigator: S.Banerjee
Sponsoring Agency: NSF
Duration: January 2004- August.2015
- Grant title:** "MARCO MSD Focus Center "
Principal-Investigator: S.Banerjee
Sponsoring Agency: DARPA/SRC
Duration: Sept. 2007-2012
- Grant title:** "CERA"
Principal-Investigator: S.Banerjee
Co-PIs: F.Register, R.Ruoff, E.Tutuc, A.Macdonald, D.Akinwande
Sponsoring Agency: DARPA/IBM
Duration: Sept. 2007-2012
- Grant title:** "NASCENT ERC ", 200k\$ per year
Principal-Investigator: Bonneau, Sreenivasan
Banerjee (Device Thrust Leader)
Sponsoring Agency: NSF
Duration: January 2013- Feb.2018
- Grant title:** "SWAN"
Principal-Investigator: S.Banerjee,
Other Investigators: F.Register, A.MacDonald and 15 others from 6 schools
Sponsoring Agency: SRC-NRI
Duration: 2006- Dec.2017
- Grant title:** "NSF-NNCI "
Principal-Investigator: S.Banerjee
Sponsoring Agency: NSF
Duration: Sept. 2015- August.2020

Ph.D.'s supervised:

K.Park, 1991
T.Hsu, 1991
S.Lian, Materials Science and Engineering, 1991
S.Batra, 1992
S.Yoganathan, 1992
B.Fowler, 1992
D.Kinosky, Materials Science and Engineering, 1993
S.Bhattacharaya, 1993
C.Li, 1994
L.Jung, 1994
A.Mahajan, 1994
C.Hu, 1995
I.Manna, 1995
A.Sultan, 1996
D.Samara, 1997
S.John, 1998
J.Liu, 1999
R.Sharma, 1999
E.Quinones, 1999
D.Kencke, 2000
Christine Ouyang (with Tasch), 2000
Xiangdong Chen, 2001
Taehoon Kim, 2001
Siva Mudanai (with Tasch), 2001
Geng Wang (with Tasch), 2001
Yang Chen (with Tasch), 2001
Xin Wang, 2002
Hong-Jyh Li, 2002
Sung –Bo Hwang (with Edgar), 2002
Di Li (with Tasch), 2002
Yang-Yu Fan, (with Register) 2002
Zhonghai Shi, 2002
Tat Ngai, 2002
Dong-Won Kim, 2003
Xiao Chen (with Rabenberg), 2003
Puneet Kohli, Fall 2003
David Onsongo, Spring 1999 - Fall 2003
Kartik Jayanarayan, Spring 2004
Tongsheng Xia, (with Register), Spring 2005
Taras Kirichenko (with Hwang), Spring 2005
James Chen, 2005
Swaroop Ganguly (with MacDonald), 2006
Fei Lei (with Register), 2006
Li Lin (2006)
Sagnik Dey (2006)
X.Fan (with Register) 2006

Y.Liu (2006)
 D.Kelly (2006)
 *Fan, Xiaofeng, Fall 2006
 Ghosh, Bahniman, Spring 2007
 Joshi, Sachin Vineet, Spring 2007
 Kelly, David Quest, Fall 2006
 Liu, Yueran, Fall 2006
 Sarkar, Joy, Fall 2007
 Donnelly, Joseph, Spring 2009
 Shahrjerdi, Davood, Fall 2008
 Tang, Shan, Fall 2008
 Zaman, Rownak, Fall 2008
 Kong, Ning, Fall 2009
 Kim, Yonghyun, Spring 2010
 Liu, Hai, Spring 2010
 Basu, Dipanjan, 2010
 Lee, Tackhwi, 2010
 Lee, Se Hoon, 2011
 Ferdousi, Fahmida, 2011
 Jamil, Mustafa, 2011
 David, John, 2011
 Yum, Jung Hwan, 2012
 Kim, Seyoung, 2012 (with Tutuc)
 Chang, Jiwon, 2013 (with Register)
 Jadaun, Priyamvada, 2013 (with Register)
 Zhai, Yujia, 2013 (with Willson)
 Ramon, Michael, 2013 (with Akinwande)
 Emmanuel Oneyagam, 2014
 Sayan Saha, 2015
 U.Roy (with Register, 2015)
 Jason Mantey (2015)
 Chris Corbet (with Tutuc, 2015)

Master's supervised:

T.Hsu, 1989
 S. Batra, 1989
 D.Bullock, 1990
 S.Bhattacharya, 1990
 B.Fowler, 1990
 K.Picone, 1991
 J.Shen, 1991 (Report Option)
 R.Kovelamudi, 1992 (Report Option)
 S.Krishnan, 1992
 L.Jung, 1992
 M.Lobo, 1992
 S.Ngaoram, 1993
 A.Khan, 1993 (Report Option)
 D.Samara, 1993
 I.Manna, 1993

A.Mahajan, 1993
 A.Sultan, 1993
 D.Khanderkar, 1993 (Report Option)
 H.Taufique, 1994 (Report Option)
 S.Madireddi, Mechanical Engineering, 1994 (Report, with I.Busch-Vishniac)
 S.John, 1995
 J.Fretwell, Materials Science & Eng., 1995 (Report, with A.Tasch)
 M.Craig, 1995
 J.Williamson, 1995
 K.Reddy, 1995
 J.Damiano, 1995
 R.Gupta, 1995
 D.Kencke, 1996
 J.Zaman, 1996
 E.Quinones, 1996
 K.Hassan, 1996
 A.Lentvorski, 1997 (Report)
 S.Oswal, 1998
 C.Seal, 1998
 V.Agarwal, 1999
 S.Raghu Nandan, 1999
 S.Ravi, 1999
 T.Ngai, 1999
 X.Chen, 1999
 V.Medina, 1999
 H.Rahman, 1999
 C.Twu, 2000
 Stimit Oak, 2001
 Gaurav Shrivastava, 2001
 Wanqiang Chen, 2001
 Swaroop Ganguly, 2001
 Taras Kirichenko, 2002
 Randall Deppensmith, 2002
 Mukund Swaminathan, 2002
 Li Lin, 2003
 Sachin Joshi, ECE-MFG, Fall 2004
 David Kelly, Fall 2003
 Doreen Ahmad, 2005
 Sachin Joshi, 2006
 Isaac M Wiedmann, Fall 2005
 Sowmya Ramachandran, Fall 2005
 Kong, Ning, Spring 2007
 Lee, Se Hoon, Spring 2007
 Nanda, Aditi Kartik, Spring 2007
 Ferdousi, Fahmida, Spring 2008
 Jain, Nitesh, Spring 2008
 Jamil, Mustafa, Spring 2008

Jayan, Baby Reeja, Spring 2008
Kim, Seyoung, Summer 2008
Onyegam, Emmanuel U., Fall 2007
Vora, Nikhil Sudhir, Spring 2008
Chang, Jiwon, Spring 2009
Jadaun, Priyamvada, Summer 2009
Varahramyan, Kamran, Fall 2008
Kaur, Shagandeep, Spring 2010
Zhai, Yu-Jia, Spring 2010
Saha, Sayan, 2010
Rik Dey, 2014
Nima, Asoudegi, 2015

Postdocs: Samit Ray, Mark Loewe, Amitava Das, Sabrina Grannan, Freek Prins, W.C.Jung, M.Palard, C.Mao, Bhagawan Sahu, Mathew Gilbert, J.Lee, D.Ahn, Domingo Ferrer, Samaraesh Gucchait, Aparna Gupta, Anupam Roy, Sushant Sonde, Sarmita Majumdar, Bahniman Ghosh, Rudy Ghosh

In progress:

Corbet, Christopher
Mantey, Jason
Onyegam, Emmanuel
Ramon, Michael
Hema Chandra Mova
Yu-jia Zhai
Urmimala Roy
Nima Assoudeghi
William Hsu
Dax Crum
Sangwoo Kang

Books and Invited Book Chapters:

1. Solid State Electronic Devices, 5th Ed. (2000), 6th Ed. (2005), 7th Ed. (2015), Prentice-Hall by B.Streetman and S.Banerjee
2. Effect of Surface Nitridation on the Electrical Characteristics of Germanium High- κ /Metal Gate Metal-Oxide-Semiconductor Devices, D. Q. Kelly, J. J.-H. Chen, S. Guha, and S. K. Banerjee. Invited Book chapter, Springer, 2007.
3. SiGe HFETs, S.Banerjee, The Silicon Heterostructure Handbook, 2005, Edited by John Cressler.
4. High-k Gate Dielectrics, Y.Fan. S.Mudanai, L. Register and S.Banerjee, 2003
5. Device Miniaturization and Simulation, S.Banerjee and B.Streetman in ULSI Devices, John Wiley, 2000 (C.Chang and S.Sze editors)
6. Dopant Diffusion, S.Banerjee in Handbook of Semiconductor Manufacturing Technology, Marcel Dekker, 2000, 2006 (Y.Nishi, B.Doering and J.Kilby editors).
7. Silicon-germanium Devices, S.Banerjee, Elsevier, 2001.
8. Novel 3D CMOS, S.Dey and S.Banerjee, Solid State Electronics Trends, 2009
9. X. Mou, L. F. Register and S. K. Banerjee, "Ultra-low-power pseudospintronics devices via exciton condensation in coupled two-dimensional material systems," in Nanoscale Materials and Devices for Electronics, Photonics and Solar Energy, Ed. Stephen Goodnick, Anatoli Korkin and Robert Nemanich, Springer, 2015
10. D. Reddy, L. F. Register and S. K. Banerjee, "Bilayer pseudoSpin Field Effect Transistor (BiSFET)" in "Beyond CMOS Logic Switches," T.-J. King and K. Kuhn, Eds., Cambridge: Cambridge Univ. Press, 2015.

Patents:

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622. * S.Banerjee, Computational Aspects of Nanowire FETs, NCN NRI Meeting, Indianapolis, Feb. 2007, **Invited**.
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624. * S.Banerjee (with N.Peppas and K.Roy), How Microelectronics will Impact and Improve Drug Discovery and Delivery, Plenary Talk, Pharma Conf. Austin, Jan. 2007.
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