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Table with 5 columns: APPLICATION NO., FILING DATE, FIRST NAMED INVENTOR, ATTORNEY DOCKET NO., CONFIRMATION NO. Includes application details for 15/215,041 and 67251, inventor Thomas Knisley, and examiner TUROCY, DAVID P.

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UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE PATENT TRIAL AND APPEAL BOARD

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*Ex parte* THOMAS KNISLEY and DAVID THOMPSON

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Appeal 2019-002041  
Application 15/215,041  
Technology Center 1700

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Before LINDA M. GAUDETTE, CHRISTOPHER L. OGDEN, and  
DEBRA L. DENNETT, *Administrative Patent Judges*.

GAUDETTE, *Administrative Patent Judge*.

DECISION ON APPEAL<sup>1</sup>

The Appellant<sup>2</sup> appeals under 35 U.S.C. § 134(a) from the Examiner's decision finally rejecting claims 7, 9, and 12–20.<sup>3</sup>

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<sup>1</sup> This Decision includes citations to the following documents: Specification filed July 20, 2016 (“Spec.”); Final Office Action dated May 14, 2018 (“Final”); Advisory Action dated July 23, 2018 (“Advisory”); Appeal Brief filed Oct. 8, 2018 (“Appeal Br.”); Examiner’s Answer dated Nov. 19, 2018 (“Ans.”); and Reply Brief filed Jan. 14, 2019 (“Reply Br.”).

<sup>2</sup> We use the word “Appellant” to refer to “applicant” as defined in 37 C.F.R. § 1.42. The Appellant identifies the real party in interest as Applied Materials, Inc. Appeal Br. 3.

<sup>3</sup> We have jurisdiction under 35 U.S.C. § 6(b).

We AFFIRM IN PART and enter a new ground of rejection pursuant to 37 C.F.R. § 41.50(b).

### CLAIMED SUBJECT MATTER

The claims are directed to methods of using heteroleptic diazadiene (“DAD”)-containing tungsten precursors for thin film deposition. Spec. ¶¶ 2, 13. The precursors used in the inventive method include a neutral donor (“ND”), such as carbonyl (“CO”), and an anionic or dianionic metallorganic ligand, such as cyclopentadienyl (“Cp”). *Id.* ¶ 13. The inventive methods utilize atomic layer deposition (“ALD”) or chemical vapor deposition (“CVD”) techniques. *See id.* ¶ 45. ALD “refers to the sequential exposure of two or more reactive compounds to deposit a layer of material on a substrate surface.” *Id.* ¶ 15.

Claim 7, reproduced below, is illustrative of the claimed subject matter:

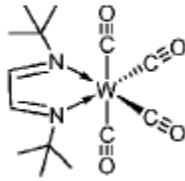
7. A processing method comprising sequentially exposing a substrate to a first reactive gas comprising a tungsten-containing compound comprising a compound with the representative formula  $W(ND)_x(DAD)_yR_z$ , where each ND is a neutral donor, each DAD is a diazadiene, each R is an anionic or dianionic ligand and x is in the range of 1 to 4, y is in the range of 1 to 3, z is in the range of 1 to 4 and  $x+z$  is greater than 1 and a second reactive gas to form a tungsten-containing film.

Appeal Br. 28 (Claims Appendix). Claim 17, the only other independent claim on appeal, differs substantively from claim 7 in that it does not require “sequential” exposure to the first and second reactive gasses. *See id.* at 29.

## REFERENCES

The Examiner relies on the following prior art as evidence of unpatentability:

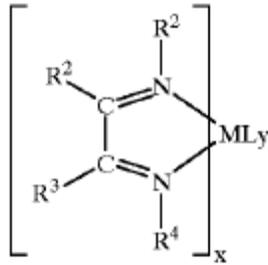
Li (WO 2014/052642 A1, published April 3, 2014) discloses a tungsten precursor for use in CVD and ALD. Li ¶ 29. Li's precursor has the following chemical structure (*id.* ¶ 7):



Above is the chemical structure of the fourth of twelve tungsten precursors identified by Li as suitable for use in a method of forming a tungsten or a tungsten-containing film on a substrate. *Id.* ¶¶ 7, 9.

Vaartstra (US 6,281,124 B1, issued August 28, 2001) discloses “a method of forming a metal-containing film using one or more complexes of Formula (I): [(R<sup>1</sup>)NC(R<sup>2</sup>)C(R<sup>3</sup>)N(R<sup>4</sup>)]<sub>x</sub>ML<sub>y</sub>” (Vaartstra 3:47–51), known as diazadiene or diazabutadiene complexes (*id.* at 2:41–42). “The complexes . . . are particularly suitable for use in a [CVD] system.” *Id.* at 1:10–12. Vaartstra discloses that “M is a Group IVB, VB, or VIB metal” (*id.* at 3:53) such as tungsten (*id.* at 1:65); “each R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> group is independently H or an organic group . . . ; L is selected from the group of CO, NO, CN, CS, CNR<sup>5</sup>, R<sup>6</sup>CN, or R<sup>7</sup>, wherein each R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> group is independently an organic group, (. . . more preferably, R<sup>7</sup> is cyclopentadienyl); x=1 to 4 . . . ; and y=1 to 4” (*id.* at 3:53–60). Vaartstra discloses that the ligand [(R<sup>1</sup>)NC(R<sup>2</sup>)C(R<sup>3</sup>)N(R<sup>4</sup>)] typically bonds to central

metal M through the nitrogen atoms as shown in the chemical structure below (*id.* at 5:21–33):



Above is the chemical structure of Vaartstra's precursor.

Shenai-Khatkhate (US 8,012,536 B2, issued September 6, 2011) discloses a method of forming a metal-containing layer on a substrate using CVD or ALD. Shenai-Khatkhate 1:8–11, 2:21–22. Shenai-Khatkhate discloses that the organometallic compounds used in the method, known generally as formamidinates or formidinate compounds, contain a metal, at least one formamidate ligand, and at least one anionic ligand. *Id.* at 3:7–10. The compounds have the formula  $(R^1NC(H)NR^2)_nM^{+m}L^1_{(m-n)}L^2_p$ . *Id.* at 3:31–32. Shenai-Khatkhate discloses that suitable metals (M) include tungsten, a wide variety of anionic ligands ( $L^1$ ) may be used including cyclopentadienyls, and neutral ligands ( $L^2$ ) include CO. *Id.* at 3:63–67, 4:4–11, 42–46. Shenai-Khatkhate discloses that anionic ligands provide increased bonding interaction as compared to a corresponding neutral ligand. *Id.* at 3:10–13.

Lansalot-Matras (US 2014/0235054 A1, published August 21, 2014) discloses tungsten diazabutadiene precursors that are suitable for use in depositing a tungsten-containing film, such as tungsten silicide, using CVD or ALD. Lansalot-Matras ¶¶ 2–3, 43. Lansalot-Matras discloses that the DAD ligands may be neutral, mono-anionic, or dianionic. *Id.* ¶ 25.

## REJECTIONS<sup>4</sup>

1. Claims 7 and 13–20 are rejected under 35 U.S.C. § 103 as unpatentable over Li and Vaartstra (“Ground 1”).
2. Claims 9 and 12 are rejected under 35 U.S.C. § 103 as unpatentable over Li and Vaarstra in view of Lansalot-Matras (“Ground 2”).
3. Claims 7 and 13–20 are rejected under 35 U.S.C. § 103 as unpatentable over Li, Vaartstra, and Shenai-Khatkhate (“Ground 3”).
4. Claims 9 and 12 are rejected under 35 U.S.C. § 103 as unpatentable over Li, Vaarstra, and Shenai-Khatkhate in view of Lansalot-Matras (“Ground 4”).
5. Claims 7 and 13–20 are rejected under 35 U.S.C. § 103 as unpatentable over Vaartstra and Shenai-Khatkhate (“Ground 5”).
6. Claims 7, 9, and 12–20 are rejected under 35 U.S.C. § 103 as unpatentable over Vaartstra and Lansalot-Matras (“Ground 6”).

## OPINION

### *Grounds 1, 2, and 6*

In each of Grounds 1, 2, and 6, the Examiner relied on Vaartstra for a teaching or suggestion of a tungsten precursor comprising DAD ligands and both CO and Cp ligands. Final 7, 9–11. The Appellant directs us to disclosure in Vaarstra to support its argument that Vaarstra discloses a DAD ligand in combination with *either* a neutral donor (e.g., CO) *or* an anionic/dianionic ligand (e.g., Cp), but does not disclose or suggest a

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<sup>4</sup> The Examiner withdrew the final rejection of claims 7, 9, and 12–20 under 35 U.S.C. § 112(b) or 35 U.S.C. § 112 (pre-AIA), second paragraph. *See* Advisory 1; Ans. 3.

precursor comprising both a neutral donor and an anionic/dianionic ligand.  
Appeal Br. 12, 18, 23; *see* Vaartstra 2:20–30, 5:12–38.

In the Answer, the Examiner asserts that “all the claimed elements were known in the prior art and one skilled in the art *could have combined* the elements as claimed by known methods with no change in their respective functions.” Ans. 9 (emphasis added). The Examiner further responds to Appellant’s arguments as follows:

the Appellant appear[s] to continually argue that Vaarstra does not disclose a DAD must include both a neutral donor and an anionic or dianionic[ ]ligand. The examiner agrees and cites Shenai-Khatkhate as to reasons why one would include in a tungsten organometallic precursor both a neutral donor (stabilizer) as well as an anionic[ ]ligand.

Ans. 17.

“[A] patent composed of several elements is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art.” *KSR Int’l Co. v. Teleflex Inc.*, 550 U.S. 398, 418 (2007). Given the Examiner’s failure to explain sufficiently why one of ordinary skill in the art, absent consideration of Shenai-Khatkhate’s disclosure, would have included both a neutral donor and an anionic/dianionic ligand in Li’s or Vaartstra’s precursor, we agree with the Appellant that the Examiner has not met the burden to show that (1) claims 7 and 13–20 would have been obvious over Li and Vaartstra, (2) claims 9 and 12 would have been obvious over Li, Vaarstra, and Lansalot-Matras, and (3) claims 7, 9, and 12–20 would have been obvious over Vaartstra and Lansalot-Matras. Accordingly, we do not sustain Grounds 1, 2, and 6.

*Ground 3*

The Examiner rejected claims 7 and 13–20 under 35 U.S.C. § 103 as unpatentable over Li, Vaartstra, and Shenai-Khatkhate. *See generally* Final 6–8. The Appellant relies on the same arguments in support of patentability of independent claims 7 and 17, and dependent claims 18–20. *See* Appeal Br. 11–17. The Appellant presents separate arguments in support of patentability of claims 13–16. *See id.* at 16.

The Examiner found that Li discloses a processing method that includes steps of exposing a substrate to a first reactive gas comprising a tungsten DAD precursor with CO ligands (a neutral donor) and to a second gas to form a tungsten-containing film. Final 6 (citing Li ¶¶ 7, 9, 29). The Examiner found that Vaartstra discloses vapor deposition of a film using tungsten precursors with a DAD ligand as well as an L group such as CO or an anionic/dianionic ligand (e.g., Cp). *Id.* at 7. The Examiner found that Shenai-Khatkhate discloses an organometallic precursor with a heteroleptic structure that includes an anionic ligand of Cp and a stabilizer of CO. *Id.* The Examiner determined that the collective teachings of the references suggest modifying Li's tungsten DAD precursor to include both Cp and CO ligands. *See id.*

The Appellant argues that formamidinate ligands, such as those described in Shenai-Khatkhate, differ vastly from DAD ligands in both chemical structure and chemical properties. Appeal Br. 14. The Appellant thus contends that in considering improvements to methods of producing tungsten films using diazadienyl-containing tungsten precursors, the ordinary artisan would not have looked to Shenai-Khatkhate. *Id.* at 14–15.

The Appellant's argument is not persuasive. To the extent the Appellant is arguing that Shenai-Khatkhate is non-analogous art, we note that "[t]wo separate tests define the scope of analogous prior art: (1) whether the art is from the same field of endeavor, regardless of the problem addressed and, (2) if the reference is not within the field of the inventor's endeavor, whether the reference still is reasonably pertinent to the particular problem with which the inventor is involved." *In re Klein*, 647 F.3d 1343, 1348 (Fed. Cir. 2011) (quoting *In re Bigio*, 381 F.3d 1320, 1325 (Fed. Cir. 2004)). The Appellant has not provided persuasive evidence to refute the Examiner's finding that Shenai-Khatkhate is at least reasonably pertinent to the problem with which the inventors were concerned.

As explained by the Examiner, like the present invention, Shenai-Khatkhate relates to CVD/ALD organometallic precursors with tungsten as the central metal atom, and both DAD and formadinate are formed from two nitrogens separated by carbon atoms, both nitrogen atoms being bonded to the tungsten. Ans. 13. Like the present inventors, Shenai-Khatkhate is concerned with thermally stable precursors that produce tungsten films containing low levels of contaminants. *Compare* Spec. ¶ 6, *with* Shenai-Khatkhate 9:15–30; *see* Ans. 11. Further, the Appellant has not provided persuasive argument or evidence (*see generally* Reply Br.) to refute the Examiner's finding that the ordinary artisan would have included an anionic ligand in Li's organometallic precursor based on Shenai-Khatkhate's disclosure that the use of only a single ligand group offers less control over achieving required thermal stability for the precursor, and that anionic ligands "provide increased bonding interaction as compared to the neutral ligand" (Ans. 11; *see* Shenai-Khatkhate 1:44–50, 3:11–13).

Accordingly, we sustain the rejection of claims 7 and 17–20 as unpatentable over the combination of Li, Vaartstra, and Shenai-Khatkhate.

As to claims 13–16, the Appellant notes that these claims depend from claim 9, which was not rejected over the combination of Li, Vaartstra, and Shenai-Khatkhate. *See* Appeal Br. 15. Claim 9 recites “wherein the second reactive gas comprises a silicon-containing compound and the tungsten-containing film comprises tungsten silicide ( $WSi_x$ ).” *Id.* at 28 (Claims Appendix). The Examiner did not identify a teaching or suggestion of these features in Li, Vaartstra, Shenai-Khatkhate, or a combination of these references, but relied on Lansalot-Matras for a teaching of forming tungsten silicide and using a silicon precursor *See* Final 8; Ans. 15.

Accordingly, we do not sustain the rejection of claims 13–16 as unpatentable over the combination of Li, Vaartstra, and Shenai-Khatkhate.

*Ground 4 and New Ground*

The Examiner rejected claims 9 and 12 under 35 U.S.C. § 103 as unpatentable over Li, Vaartstra, Shenai-Khatkhate, and Lansalot-Matras. *See generally* Final 8–9. As indicated above, in rejecting claim 9, the Examiner determined that using a silicon-containing compound as the second reactive gas in the modified method of Li to produce a film comprising tungsten silicide ( $WSi_x$ ) would have been obvious in view of Lansalot-Matras’s disclosure. Final 8 (citing Lansalot-Matras ¶¶ 8, 16, 43, 46).

Claim 12 depends from claim 9 and recites a specific formula for at least one DAD ligand of the tungsten-containing compound used in the claimed method. Appeal Br. 28 (Claims Appendix). Specifically, claim 12 requires that the DAD ligand consist of a doubly anionic system where both nitrogen atoms are capable of being covalently bound to the tungsten atom

and that each of two R groups is independently selected from a limited list that includes C1-C6 alkyl groups. *Id.* The Examiner found that Lansalot-Matras discloses using a doubly anionic system with R1 and R6 being C1-C6 linear alkyls. Ans. 8 (citing Lansalot-Matras ¶¶ 24–25, 52). The Examiner determined that modifying Li’s tungsten DAD precursor to include a DAD ligand as disclosed in Lansalot-Matras would have been obvious to one of ordinary skill in the art. *Id.*

The Appellant’s arguments in support of patentability of claims 9 and 12 are limited to a contention that the ordinary artisan would not have looked to Lansalot-Matras because the compounds described therein are homoleptic—they “contain 3 DAD ligands and no other ligands complexed to tungsten”—whereas the claimed invention relates to heteroleptic metal compounds. Appeal Br. 18–19. The Appellant explains that “a metal species having more than one type of ligand is heteroleptic, while a metal species having all ligands identical is homoleptic.” *Id.* at 18. The Appellant argues that “[h]eteroleptic and homoleptic metal compounds are distinct in their chemical properties, such that one skilled in the art would not expect one to be informative of the other.” *Id.*

The Appellant has not identified persuasive evidence to support this argument and, therefore, we are not persuaded of reversible error in the Examiner’s obviousness determination as to claims 9 and 12. *See In re Geisler*, 116 F.3d 1465, 1471 (Fed. Cir. 1997) (explaining that argument by counsel cannot take the place of evidence). Accordingly, we sustain the rejection of claims 9 and 12 as unpatentable over the combination of Li, Vaartstra, Shenai-Khatkhate, and Lansalot-Matras.

Claims 13–16 depend from claim 9. *See* Appeal Br. 28 (Claims Appendix). As discussed in the preceding paragraphs, the Appellant has not shown reversible error in the Examiner’s determination that claim 9 is unpatentable over the combination of Li, Vaartstra, Shenai-Khatkhate, and Lansalot-Matras. The Examiner found, and the Appellant does not dispute, that Li, Vaartstra, Shenai-Khatkhate, or a combination thereof, teach or suggest the additional limitations recited in each of claims 13–16. *See* Final 7–8; Appeal Br. 16. Accordingly, we enter a new ground of rejection of claims 13–16 under 35 U.S.C. § 103 as unpatentable over Li, Vaartstra, Shenai-Khatkhate, and Lansalot-Matras.

*Ground 5*

The Examiner rejected claims 7 and 13–20 under 35 U.S.C. § 103 as unpatentable over Vaartstra and Shenai-Khatkhate. *See generally* Final 9–10. The Examiner found that Vaartstra discloses a method of forming a tungsten-containing film comprising sequentially exposing a substrate to first and second reactive gases. *Id.* at 9. The Examiner found that Vaartstra discloses that the first reactive gas comprises a tungsten precursor with a DAD ligand as well as an L group such as CO or Cp. *Id.* The Examiner found that Shenai-Khatkhate discloses an organometallic precursor with a heterolopetic structure that includes an anionic ligand of Cp and a stabilizer of CO. *Id.* at 10. The Examiner determined that given Shenai-Khatkhate’s disclosure, using a tungsten precursor with a DAD ligand and both Cp and CO ligands in Vaarstra’s method would have been obvious to one of ordinary skill in the art. *Id.*

The Appellant’s arguments are substantially the same as those made in support of patentability of the claims over the combination of Li,

Vaartstra, and Shenai-Khatkhate. *Compare* Appeal Br. 19–22, *with id.* at 11–17. For the reasons discussed above, these arguments fail to identify error in the Examiner’s rejection of claims 7 and 17–20, but are persuasive of reversible error in the Examiner’s rejection of claims 13–16.

Accordingly, we sustain the rejection based on the combination of Vaartstra and Shenai-Khatkhate as to claims 7 and 17–20, but reverse as to claims 13–16.

### CONCLUSION

Claims Rejected	35 U.S.C. §	Reference(s)/Basis	Affirmed	Reversed	New Ground
7, 13–20	103	Li, Vaartstra		7, 13–20	
9, 12	103	Li, Vaartstra, Lansalot-Matras		9, 12	
7, 13–20	103	Li, Vaartstra, Shenai-Khatkhate	7, 17–20	13–16	
9, 12–16	103	Li, Vaartstra, Shenai-Khatkhate, Lansalot-Matras	9, 12		13–16
7, 13–20	103	Vaartstra, Shenai-Khatkhate	7, 17–20	13–16	
7, 9, 12–20	103	Vaartstra, Lansalot-Matras		7, 9, 12–20	
<b>Overall Outcome</b>			7, 9, 12, 17–20	13–16	13–16

37 C.F.R. § 41.50(b) provides that an appellant, WITHIN TWO MONTHS FROM THE DATE OF THE DECISION, must exercise one of the following two options with respect to the new grounds of rejection to avoid termination of the appeal as to the rejected claims:

- (1) *Reopen prosecution.* Submit an appropriate amendment of the claims so rejected or new

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Evidence relating to the claims so rejected, or both, and have the matter reconsidered by the examiner, in which event the prosecution will be remanded to the examiner. . . .

(2) *Request rehearing*. Request that the proceeding be reheard under § 41.52 by the Board upon the same Record.

No time period for taking any subsequent action in connection with this appeal may be extended under 37 C.F.R. § 1.136(a)(1)(iv). *See* 37 C.F.R. § 41.50(f) (2012).

AFFIRMED IN PART;  
37 C.F.R. § 41.50(b)