

DESCRIPTION

METHOD OF FORMING A Ta₂O₅ COMPRISING LAYER

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TECHNICAL FIELD

This invention relates to methods of forming Ta₂O₅ comprising layers.

BACKGROUND ART

10 As DRAMs increase in memory cell density, there is a continuing challenge to maintain sufficiently high storage capacitance despite decreasing cell area. Additionally, there is a continuing goal to further decrease cell area. One principal way of increasing cell capacitance is through cell structure techniques. Such techniques include three-
15 dimensional cell capacitors, such as trenching or stacked capacitors. Yet as feature size continues to become smaller and smaller, development of improved materials for cell dielectrics as well as the cell structure are important. Highly integrated memory devices are expected to require a very thin dielectric film for the 3-dimensional capacitor of cylindrically stacked or
20 trenching structures. To meet this requirement, the capacitor dielectric film thickness may be at or below 10 Angstroms of equivalent SiO₂ thickness.

Insulating inorganic metal oxide materials (such as ferroelectric materials, perovskite materials and dielectric oxides) are commonly referred to as "high k" materials due to their high dielectric constants, which make
25 them attractive as dielectric materials in capacitors, for example for high density DRAMs and non-volatile memories. Using such materials can enable the creation of much smaller and simpler capacitor structures for a given stored charge requirement, enabling the packing density dictated by future circuit design. One such material is tantalum pentoxide (Ta₂O₅).
30 Ta₂O₅ can, of course, also be used in fabrication of materials other than capacitor dielectrics and in circuitry other than DRAM.

The dielectric constant of tantalum pentoxide can vary in a range from about 25 to in excess of 100. Typical prior art methods of forming tantalum pentoxide result in an initial deposition in the amorphous phase, and which
35 also results in dielectric constants in the lowest portions of the range. Accordingly, subsequent anneal processes are typically employed to convert the material to various crystalline phases to achieve a significantly higher

dielectric constant than the amorphous phase. Typical amorphous deposition processes include low pressure chemical vapor deposition utilizing tantalum organometallics. One inorganic process for depositing amorphous tantalum pentoxide utilizes chemical vapor deposition that is plasma enhanced using TaF₅ with an O₂/H₂ plasma.

While the invention was motivated in addressing the above issues and improving upon the above-described drawbacks, it is in no way so limited. The invention is only limited by the accompanying claims as literally worded (without interpretative or other limiting reference to the above background art description, remaining portions of the specification or the drawings) and in accordance with the doctrine of equivalents.

SUMMARY

The invention includes methods of forming Ta₂O₅ comprising layers. In one implementation, such includes positioning a substrate within a deposition chamber. Gaseous precursors comprising TaF₅ and at least one of H₂O and O₃ are fed to the deposition chamber under conditions effective to deposit a Ta₂O₅ comprising layer on the substrate.

In one implementation, a substrate is positioned within a deposition chamber. A first species is chemisorbed onto the substrate within the chamber to form a first species monolayer from a gaseous first precursor comprising TaF₅. The chemisorbed first species is contacted with a gaseous second precursor comprising at least one of H₂O and O₃ to react with the first species to form a monolayer comprising Ta and O. The chemisorbing and contacting are successively repeated under conditions effective to form a mass of material on the substrate comprising Ta₂O₅.

Other aspects and implementations are contemplated.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic depiction of a processing chamber having a substrate positioned therein.

Fig. 2 is a diagrammatic depiction of a substrate fragment.

Fig. 3 is a diagrammatic depiction of another substrate fragment.

Fig. 4 is a diagrammatic depiction of still another substrate fragment.

Fig. 5 is a diagrammatic depiction of yet another substrate fragment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 An exemplary method of forming a Ta₂O₅ comprising layer on a substrate is described initially with reference to Fig. 1. Diagrammatically shown is a deposition chamber 10 within which a substrate 12, for example a semiconductor substrate, has been positioned. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate"
10 is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any
15 supporting structure, including, but not limited to, the semiconductive substrates described above.

Gaseous precursors comprising TaF₅ and at least one of H₂O and O₃ are fed to deposition chamber 10 under conditions effective to deposit a Ta₂O₅ comprising layer 14 upon substrate 12. Such might be conducted
20 by atomic layer deposition (ALD) methods (for example including chemisorbing and contacting methods), by chemical vapor deposition methods (CVD), by other methods, as well as by a combination of these and other methods. CVD and ALD are used herein as referred to in the co-pending U.S. Patent Application Serial No. 10/133,947, filed on April 25,
25 2002, entitled "Atomic Layer Deposition Methods and Chemical Vapor Deposition Methods", and listing Brian A. Vaartstra as the inventor. This 10/133,947 application filed on April 25, 2002 is hereby fully incorporated by reference as if presented in its entirety herein.

Fig. 1 diagrammatically depicts separate TaF₅ and one or both of H₂O
30 and O₃ precursor feed streams to chamber 10. More or fewer precursor feed streams could be provided, of course. Further, feed streams might be combined and mixed prior to feeding to chamber 10. An exemplary vacuum controlling drawdown/exhaust line 16 extends from chamber 10 for exhausting unreacted gas and by-product from the substrate, and for
35 controlling chamber pressure. The deposition conditions can comprise

plasma generation of at least one or all of the precursors, or be void of plasma generation of any of the precursors. Further, any such plasma generation might be within deposition chamber 10 and/or remote therefrom.

TaF₅ is a solid at room ambient conditions. Such is preferably heated
5 to a temperature of from 40°C to 110°C, and more preferably from 60°C to 80°C, thereby causing it to sublime. An inert carrier gas, for example He, can be flowed over the subliming solid to move the TaF₅ vapor to the chamber. An exemplary flow rate for the He is from 5 sccm to 400 sccm for a 14,000 cm³ volume deposition chamber. H₂O can be provided to the
10 chamber from a bubbler/vaporizer, with an exemplary flow rate for a 14,000 cm³ volume reactor being from 5 sccm to 400 sccm. In addition to or in lieu of the H₂O precursor feed, an exemplary O₃ precursor stream flow is a mixture of O₃ and O₂ at from 25 sccm to 400 sccm, with the feed stream being from 3% to 15% by weight O₃, the remainder being O₂. Such could be
15 created from any suitable existing or yet-to-be-developed ozone generator. Accordingly, the invention in one aspect also contemplates a combined feeding of O₃ and O₂ without feeding H₂O to the chamber, or in combination with H₂O. Further and regardless, the H₂O, O₃ and O₂ might separately be fed at different exclusive times, at different and partially overlapping times,
20 or in combination.

Further, the deposition conditions can include feeding TaF₅ and at least one of the H₂O and O₃ to the deposition chamber at the same time or at different respective times. Further when flowed at different respective times, some of the TaF₅ and at least one of the H₂O and O₃ feedings might
25 overlap in time or not overlap in time.

Preferred conditions include a substrate temperature of from about 200°C to about 400°C, more preferably from about 250°C to about 300°C, and even more preferably at a temperature of at least 275°C. The deposition conditions are also preferably subatmospheric, with a preferred
30 pressure range being from about 1 x 10⁻⁷ Torr to about 10 Torr, and more preferably from about 1 x 10⁻³ Torr to about 10 Torr.

Regardless, the conditions are preferably effective to form at least a majority of the Ta₂O₅ to be crystalline in the 001 oriented hexagonal phase as initially deposited, and regardless of whether the outer surface of
35 substrate 12 upon which the material is deposited is substantially crystalline

or substantially amorphous. In the context of this document, "substantially crystalline" and "substantially amorphous" define a layer having at least 90% of the stated crystalline or amorphous attribute. In a less preferred embodiment, the deposition might form less than a majority of the Ta₂O₅ to be crystalline in a 001 oriented hexagonal phase as initially deposited. In such less preferred embodiment, the substrate with initially deposited layer might then be annealed at a temperature of from about 400°C to 800°C effective to form at least a majority of the Ta₂O₅ to be crystalline in a 001 oriented hexagonal phase. Such annealing might occur in the same or a different chamber than which the initial deposition occurred.

Where the conditions comprise feeding TaF₅ and at least one of H₂O and O₃ to the deposition chamber at different respective times, the conditions might be void of any inert purge gas feeding to the chamber at any time intermediate such different respective times. Alternately by way of example only, the conditions might comprise a period of time intermediate the different respective times when no detectable gaseous precursor is fed to the chamber, and with an inert purge gas being fed to the chamber during at least some of that intermediate period of time. Regardless and in one preferred method, the conditions are void of any detectable level of H₂ being fed to the deposition chamber.

One exemplary reduction-to-practice example utilized/resulted in CVD in the absence of plasma in a pulsed precursor method with the conditions comprising reaction of the gaseous TaF₅ and at least one of H₂O and O₃ within the chamber and subsequently depositing material comprising Ta₂O₅ on the substrate. Specifically, Ta₂O₅ was deposited using TaF₅ and separate water vapor/steam pulses to form an 1800 Angstroms layer of Ta₂O₅ after 550 cycles, and which was in a highly 001 oriented hexagonal phase as-deposited and had less than two atomic percent fluorine. Substrate temperature was 275°C. The TaF₅ pulses were unmetered from a 70°C reservoir for 1 second long each, and the H₂O pulses were 10 sccm for 1 second long each. The reactor was purged with argon (30 sccm) for 1 second and pumped out for 2 seconds after each of the TaF₅ and ozone pulses. The purging/pumping was apparently not effective in removing all excess water vapor in light of a non-limiting, CVD rate of deposition being obtained.

Preferred pulse times for the TaF_5 vapor are from 0.1 second to 5 seconds, and more preferably from 0.2 second to 2 seconds. Preferred pulse times for the H_2O and/or O_3 vapor are from 0.1 second to 10 seconds, and more preferably from 1 second to 3 seconds.

5 Exemplary atomic layer deposition methods are described with reference to Figs. 2-4. Fig. 2 depicts a substrate 20 which would be positioned within a suitable deposition chamber. A gaseous first precursor comprising TaF_5 would be fed to the substrate within the chamber to chemisorb a first species onto the substrate to form a first species
10 monolayer on the substrate. Of course, the first species monolayer may less than completely saturate the substrate surface, and thereby be discontinuous. Fig. 2 depicts an exemplary such species TaF_x , where "x" would be less than 5.

Referring to Fig. 3, the chemisorbed first species is contacted with a
15 gaseous second precursor comprising at least one of H_2O and O_3 to react with the first species to form a monolayer comprising both Ta and O. Fig. 3 depicts two such materials, Ta-O_x , where "x" would be less than 2.5 and largely result from O_3 exposure, and Ta-(OH)_y and largely result from H_2O exposure. The surface species might further be a combination of these, for
20 example $\text{Ta(O)}_x(\text{OH})_y$. A first species is chemisorbed onto the substrate within the chamber to form a first species monolayer from a gaseous first precursor comprising TaF_5 .

Fig. 4 depicts subsequent exposure to a gaseous first precursor comprising TaF_5 , again resulting in a first species chemisorbing and
25 transformation of the TaO_x and Ta(OH)_y to a growing Ta_2O_5 mass. Accordingly, and by way of example only, such chemisorbing and contacting can be successively repeated under conditions which are effective to form a mass of material on the substrate comprising, consisting essentially of, or consisting of Ta_2O_5 . Preferred and exemplary processing conditions are
30 otherwise as described above, where applicable. Most preferably, the successive repeating is effective to form at least a majority of the Ta_2O_5 to be crystalline in the 001 oriented hexagonal phase, as initially deposited.

Further in one preferred embodiment, a period of time might be provided intermediate the chemisorbing and the contacting wherein no
35 detectable gaseous precursor is fed to the chamber and with, if desired, an

inert purge gas being fed to the chamber during such intermediate period of time or times. Further, the gaseous first or second precursors might be changed in composition, as selected by the artisan, one or more times during the successive repeating of chemisorbing and contacting. Further, the first species might be formed continuously or discontinuously over the substrate. Further if desired after at least some of the successively repeating, deposition mechanism might be switched to CVD, or start with CVD and switch to ALD. Regardless, the deposited mass might comprise, consist essentially of, or consist of Ta_2O_5 formed on the substrate.

Fig. 5 depicts but one exemplary preferred application in the fabrication of a substrate 50. Such comprises some base substrate material or materials 52 having a capacitor construction 54 formed thereon. Capacitor 54 includes first and second capacitor electrodes 56 and 58, respectively, having a capacitor dielectric region 75 sandwiched therebetween. Some or all of capacitor dielectric region 75 preferably comprises Ta_2O_5 deposited by any of the above-described methods. Exemplary reduction-to-practice capacitors fabricated in the above manners have shown dielectric constants near 100, with leakage in the high 10^{-8} amps/cm² range. One exemplary specific example utilized 1000 Angstroms thick sputtered platinum capacitor electrodes having a capacitor dielectric region consisting essentially of Ta_2O_5 deposited in accordance with the above method to a film thickness of 390 Angstroms. Such a film was deposited using 1 second pulses of TaF_5 at 70°C, 0.5 second pulses of H_2O vapor at 16°C at 5 sccm, 1 second argon purge pulses at 30 sccm and 3 seconds pumping thereafter intermediate the TaF_5 and H_2O pulses, a substrate temperature of 250°C, and 500 of each such cycles. The material had a dielectric constant of 45, and current leakage was on the order of 10^{-8} amps/cm².

An alternate exemplary and better-resulting product was obtained utilizing top and bottom electrodes 500 Angstroms thick which each comprised a combination of rhodium and platinum. The dielectric film consisted essentially of tantalum pentoxide deposited to a film thickness of 1330 Angstroms. The precursor pulses were 1 second of TaF_5 at 70°C and 0.2 seconds of H_2O at ambient room temperature conditions, with 1 second argon purge pulses at 30 sccm and 3 seconds pumping thereafter

intermediate the TaF₅ and H₂O pulses. Substrate temperature was 275°C, and the TaF₅ and H₂O pulses were conducted for 800 cycles each. The crystalline phase was predominately 001 hexagonal phase orientation, the material had a dielectric constant of about 100, and current leakage was in
5 the high 10⁻⁸ amps/cm² range.

CLAIMS

What is claimed is:

1. A method of forming a Ta₂O₅ comprising layer on a substrate,
5 comprising:
positioning a substrate within a deposition chamber; and
feeding gaseous precursors comprising TaF₅ and at least one of H₂O
and O₃ to the deposition chamber under conditions effective to deposit
a Ta₂O₅ comprising layer on the substrate.

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2. The method of claim 1 wherein the conditions are effective to
form at least a majority of the Ta₂O₅ to be crystalline in a 001 oriented
hexagonal phase as initially deposited.

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3. The method of claim 1 wherein the conditions are effective to
form less than a majority of the Ta₂O₅ to be crystalline in a 001 oriented
hexagonal phase as initially deposited, and annealing the as initially
deposited layer at a temperature of from about 400°C to 800°C effective to
form at least a majority of the Ta₂O₅ to be crystalline in a 001 oriented
20 hexagonal phase.

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4. The method of claim 1 wherein the Ta₂O₅ comprising layer is
deposited onto a substrate outer surface which is substantially crystalline,
and the conditions are effective to form at least a majority of the Ta₂O₅ to be
25 crystalline in a 001 oriented hexagonal phase as initially deposited.

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5. The method of claim 1 wherein the conditions comprise feeding
TaF₅ and at least one of H₂O and O₃ to the deposition chamber at the same
time.

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6. The method of claim 1 wherein the conditions comprise feeding
TaF₅ and at least one of H₂O and O₃ to the deposition chamber at different
respective times.

7. The method of claim 6 wherein the conditions are void of any inert purge gas feeding to the chamber at any time intermediate said different respective times.

5 8. The method of claim 6 further comprising a period of time intermediate said different respective times when no detectable gaseous precursor is fed to the chamber, an inert purge gas being fed to the chamber during at least some of said intermediate period of time.

10 9. The method of claim 6 wherein some of the TaF₅ and at least one of the H₂O and O₃ feedings overlap in time.

10. The method of claim 6 wherein neither of the TaF₅ and at least one of the H₂O and O₃ feedings overlap in time.

15 11. The method of claim 1 wherein the conditions comprise plasma generation of at least one of the precursors.

20 12. The method of claim 11 wherein the plasma generation is within the deposition chamber.

13. The method of claim 11 wherein the plasma generation is remote from the deposition chamber.

25 14. The method of claim 1 wherein the conditions are void of plasma generation of the precursors.

30 15. The method of claim 1 wherein H₂O comprises one of the gaseous precursors.

16. The method of claim 1 wherein O₃ comprises one of the gaseous precursors.

35 17. The method of claim 1 wherein the gaseous precursors comprise a combined feeding of O₃ and O₂.

18. The method of claim 1 wherein the gaseous precursors comprise H₂O and O₃.

19. The method of claim 18 wherein the conditions comprises a
5 combined feeding of the H₂O and the O₃.

20. The method of claim 1 wherein the gaseous precursors comprise H₂O, O₃, and O₂.

10 21. The method of claim 20 wherein the conditions comprises a combined feeding of the H₂O, the O₃ and the O₂.

22. The method of claim 1 wherein the conditions are void of feeding any detectable level of H₂ to the deposition chamber.
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23. The method of claim 1 wherein the conditions comprise a substrate temperature of from about 200°C to about 400°C.

24. The method of claim 1 wherein the conditions comprise a
20 substrate temperature of from about 250°C to about 300°C.

25. The method of claim 1 wherein the conditions comprise a chamber pressure of from about 1×10^{-7} to about 10 Torr.

25 26. The method of claim 1 wherein the conditions comprise a chamber pressure of from about 1×10^{-3} to about 10 Torr.

27. The method of claim 1 wherein the conditions comprise atomic layer deposition.
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28. The method of claim 1 wherein the conditions comprise chemical vapor deposition.

29. The method of claim 1 wherein the conditions comprise atomic layer deposition for a period of time and chemical vapor deposition for another period of time.

5 30. The method of claim 1 comprising fabricating the layer as at least part of a capacitor dielectric region.

31. A method of forming a Ta_2O_5 comprising layer on a substrate, comprising:

10 positioning a substrate within a deposition chamber; and
 feeding gaseous precursors comprising TaF_5 and H_2O to the deposition chamber under conditions effective to deposit a Ta_2O_5 comprising layer on the substrate having at least a majority of the Ta_2O_5 to be crystalline in a 001 oriented hexagonal phase as initially deposited.

15 32. The method of claim 31 wherein the conditions comprise feeding O_3 to the deposition chamber.

20 33. The method of claim 31 wherein the conditions comprise feeding TaF_5 and H_2O to the deposition chamber at the same time.

25 34. The method of claim 31 wherein the conditions comprise feeding TaF_5 and H_2O to the deposition chamber at different respective times.

30 35. The method of claim 34 wherein the conditions are void of any inert purge gas feeding to the chamber at any time intermediate said different respective times.

36. The method of claim 34 further comprising a period of time intermediate said different respective times when no detectable gaseous precursor is fed to the chamber, an inert purge gas being fed to the chamber during at least some of said intermediate period of time.

37. The method of claim 34 wherein some of the TaF₅ and the H₂O feedings overlap in time.

38. The method of claim 34 wherein neither of the TaF₅ and the H₂O feedings overlap in time.

39. The method of claim 31 wherein the conditions comprise plasma generation of at least one of the precursors.

40. The method of claim 39 wherein the plasma generation is within the deposition chamber.

41. The method of claim 39 wherein the plasma generation is remote from the deposition chamber.

42. The method of claim 31 wherein the conditions are void of plasma generation of the precursors.

43. The method of claim 31 wherein the conditions are void of feeding any detectable level of H₂ to the deposition chamber.

44. The method of claim 31 wherein the conditions comprise a substrate temperature of from about 200°C to about 400°C.

45. The method of claim 31 wherein the conditions comprise a substrate temperature of from about 250°C to about 300°C.

46. The method of claim 31 wherein the conditions comprise a chamber pressure of from about 1×10^{-7} to about 10 Torr.

47. The method of claim 31 wherein the conditions comprise a chamber pressure of from about 1×10^{-3} to about 10 Torr.

48. The method of claim 31 wherein the conditions comprise atomic layer deposition.

49. The method of claim 31 wherein the conditions comprise chemical vapor deposition.

50. The method of claim 31 wherein the conditions comprise atomic layer deposition for a period of time and chemical vapor deposition for another period of time.

51. The method of claim 31 comprising fabricating the layer as at least part of a capacitor dielectric region.

52. An atomic layer deposition method of forming a Ta_2O_5 comprising layer on a substrate, comprising:

positioning a substrate within a deposition chamber;

chemisorbing a first species to form a first species monolayer onto the substrate within the chamber from a gaseous first precursor comprising TaF_5 ;

contacting the chemisorbed first species with a gaseous second precursor comprising at least one of H_2O and O_3 to react with the first species to form a monolayer comprising Ta and O; and

successively repeating said chemisorbing and contacting under conditions effective to form a mass of material on the substrate comprising Ta_2O_5 .

53. The method of claim 52 further comprising a period of time intermediate said chemisorbing and contacting wherein no detectable gaseous precursor is fed to the chamber.

54. The method of claim 52 further comprising a period of time intermediate said chemisorbing and contacting wherein no detectable gaseous precursor is fed to the chamber, an inert purge gas being fed to the chamber during at least some of said intermediate period of time.

55. The method of claim 52 wherein composition of the gaseous second precursor changes at least once during the successively repeating.

56. The method of claim 52 wherein the first species is formed continuously over the substrate.

57. The method of claim 52 further comprising at least after some
5 of the successively repeating, chemical vapor depositing Ta_2O_5 onto the mass of material using the first and second gaseous precursors.

58. The method of claim 52 wherein the successively repeating is effective to form at least a majority of the Ta_2O_5 to be crystalline in a 001
10 oriented hexagonal phase as initially deposited.

59. The method of claim 52 wherein the conditions are effective to form less than a majority of the Ta_2O_5 to be crystalline in a 001 oriented hexagonal phase as initially deposited, and annealing the as initially
15 deposited layer at a temperature of from about 400°C to 800°C effective to form at least a majority of the Ta_2O_5 to be crystalline in a 001 oriented hexagonal phase.

60. The method of claim 52 wherein the Ta_2O_5 is deposited onto a
20 substrate outer surface which is substantially crystalline, and the successively repeating is effective to form at least a majority of the Ta_2O_5 to be crystalline in a 001 oriented hexagonal phase as initially deposited.

61. The method of claim 52 comprising plasma generation of at
25 least one of the first and second precursors.

62. The method of claim 61 wherein the plasma generation is within the deposition chamber.

63. The method of claim 61 wherein the plasma generation is
30 remote from the deposition chamber.

64. The method of claim 52 wherein the chemisorbing and the contacting are void of plasma generation of the precursors.

65. The method of claim 52 wherein the gaseous second precursor comprises H₂O.

5 66. The method of claim 52 wherein the gaseous second precursor comprises O₃.

67. The method of claim 52 wherein the gaseous second precursor comprises both O₃ and O₂.

10 68. The method of claim 52 wherein the gaseous second precursor comprises both H₂O and O₃.

69. The method of claim 52 wherein the gaseous second precursor comprises all of H₂O, O₃, and O₂.

15 70. The method of claim 52 wherein the chemisorbing and the contacting comprise a substrate temperature of from about 200°C to about 400°C.

20 71. The method of claim 52 wherein the chemisorbing and the contacting comprise a substrate temperature of from about 250°C to about 300°C.

25 72. The method of claim 52 wherein the chemisorbing and the contacting comprise a chamber pressure of from about 1×10^{-7} to about 10 Torr.

30 73. The method of claim 52 wherein the chemisorbing and the contacting comprise a chamber pressure of from about 1×10^{-3} to about 10 Torr.

74. The method of claim 52 comprising fabricating the layer as at least part of a capacitor dielectric region.