

CLAIMS

1. A method of etching comprising:

(a) providing a substrate including a silicon-containing film in a chamber of a plasma treatment system; and

(b) etching the silicon-containing film with a chemical species in plasma generated from a process gas in the chamber, the process gas including a phosphorus gas component, a fluorine gas component, and a hydrogen gas component containing at least one component selected from the group consisting of hydrogen fluoride, H₂, ammonia, and hydrocarbons.

2. The method of claim 1, wherein the fluorine gas component includes at least one component selected from the group consisting of a fluorocarbon gas and a carbon-free fluorine gas.

3. The method of claim 2, wherein the process gas further includes a hydrofluorocarbon gas.

4. The method of claim 2, wherein the fluorocarbon gas includes at least one fluorocarbon selected from the group consisting of CF₄, C₃F₈, C₄F₆, and C₄F₈.

5. The method of claim 4, wherein the carbon-free fluorine gas is nitrogen trifluoride gas or sulfur hexafluoride gas.

6. The method of any one of claims 1 to 5, wherein the process gas further includes a halogen gas component containing a halogen component other than fluorine component.

5 7. A method of etching comprising:

(a) providing a substrate including a silicon-containing film in a chamber of a plasma treatment system; and

(b) etching the silicon-containing film with a chemical species in plasma generated from a process gas in the chamber, the process gas including a phosphorus gas component, a fluorine gas component, a hydrofluorocarbon gas component, and a halogen gas component containing a halogen component other than fluorine component.

8. The method of claim 7, wherein the fluorine gas component includes at least one component selected from the group consisting of a fluorocarbon gas and a carbon-free fluorine gas.

9. The method of claim 8, wherein the carbon-free fluorine gas is nitrogen trifluoride gas or sulfur hexafluoride gas.

10. The method of any one of claims 6 to 9, wherein the halogen gas component is Cl_2 gas and/or HBr gas.

11. The method of any one of claims 1 to 10, wherein the ratio of the flow rate of a second gas to the flow rate of a first gas in the process gas is above 0 and 0.5 or less,

the first gas is all gases included in the process gas excluding the phosphorus gas component, and

the second gas is the phosphorus gas component.

5 12. The method of claim 11, wherein the ratio is 0.075 or more and 0.3 or less.

10 13. The method of any one of claims 1 to 12, further comprising forming a protective film containing phosphorous-oxygen bonds contained in the process gas on a side wall surface of a recess formed by the etching.

15 14. The method of any one of claims 1 to 13, wherein
Step (b) includes periodically applying pulsed bias electric power to a bottom electrode of a substrate support that supports the substrate, when the plasma is present in the chamber, and
the bias electric power is radio-frequency bias electric power or pulsed DC voltage with negative polarity.

20 15. The method of claim 14, wherein a frequency defining a period in which the pulsed bias electric power is applied to the bottom electrode is 5 Hz or higher and 100 kHz or lower.

25 16. The method of any one of claims 1 to 15, further comprising, before Step (b), setting the temperature of a substrate support that supports the substrate to 0°C or less.

17. A method of etching comprising:

(a) providing a substrate having a silicon-containing film and a mask in a chamber of a plasma treatment system; and

(b) generating plasma from a process gas in the chamber to etch the silicon-containing film, the process gas including a hydrogen fluoride gas component, a phosphorus gas component, and a carbon gas component.

18. The method of claim 17, wherein among the flow rate of the hydrogen fluoride gas component, the flow rate of the phosphorus gas component, and the flow rate of the carbon gas component, the flow rate of the hydrogen fluoride gas component is largest.

19. The method of claim 17, wherein the process gas further includes a rare gas, and among the flow rates of all gases in the process gas excluding the rare gas, the flow rate of the hydrogen fluoride gas component is largest.

20. The method of any one of claims 17 to 19, wherein in Step (b), the temperature of a substrate support that supports the substrate is set to a temperature of 0°C or less or -40°C or less.

21. The method of any one of claims 17 to 20, wherein the process gas further includes a fluorine-free halogen gas component.

22. The method of any one of claims 17 to 21, wherein the mask

includes carbon.

23. The method of any one of claims 1 to 22, wherein the silicon-containing film includes a silicon oxide film, a silicon oxide film and a silicon nitride film, or a silicon oxide film and a polycrystalline silicon film.

24. The method of any one of claims 1 to 23, wherein the phosphorus gas component includes a halogen component.

25. The method of any one of claims 1 to 23, wherein the phosphorus gas component includes at least one of PF_3 , PCl_3 , PF_5 , PCl_5 , POCl_3 , PH_3 , PBr_3 , or PBr_5 .

26. The method of any one of claims 1 to 23, wherein the phosphorus gas component includes a fluorine component.

27. The method of claim 26, wherein the phosphorus gas component includes PF_3 or PF_5 .

28. The method of any one of claims 17 to 22, wherein the carbon gas component includes at least one of fluorocarbon or hydrofluorocarbon.

29. The method of claim 28, wherein the carbon gas component includes two or more carbon atoms.

30. The method of any one of claims 1 to 29, wherein the process gas further includes an oxygen gas component.

31. The method of claim 18, wherein the proportion of the flow rate of the hydrogen fluoride gas component to the flow rate of the process gas excluding a rare gas is 50% or more and less than 99%.

32. The method of claim 17 or 18, wherein the proportion of the flow rate of the phosphorous gas component to the flow rate of the process gas excluding a rare gas is 1% or more and 20% or less.

33. The method of any one of claims 1 to 32, wherein the plasma treatment system is a capacitively coupled plasma treatment system.

34. The method of claim 33, wherein in Step (b), the plasma is generated by supplying a radio-frequency power to a bottom electrode of a substrate support configured to support the substrate in the chamber.

35. The method of claim 33, wherein the plasma treatment system includes a substrate support provided in the chamber and an upper electrode disposed above the substrate support, and

in Step (b), the plasma is generated by supplying a radio-frequency power to the upper electrode.

36. The method of claim 34 or 35, wherein a frequency of the radio-frequency power is not less than 27 MHz and not more than 100 MHz.

37. The method of any one of claims 1 to 32, wherein the plasma treatment system is an inductively coupled plasma treatment system.

5 38. A plasma treatment system comprising:

a chamber;

a substrate support provided in the chamber;

a gas supply unit configured to supply a process gas into the chamber, the process gas including a phosphorus gas component, a
10 fluorine gas component, and a hydrogen gas component containing at least one component selected from the group consisting of hydrogen fluoride, H₂, ammonia, and hydrocarbons;

a plasma generator configured to generate plasma from the process gas; and

15 a controller configured to control the gas supply unit to supply the process gas into the chamber and control the plasma generator to generate plasma from the process gas in the chamber to etch a silicon-containing film of a substrate supported by the substrate support.

20 39. The plasma treatment system of claim 38, wherein the fluorine gas component includes at least one component selected from the group consisting of a fluorocarbon gas and a carbon-free fluorine gas.

40. The plasma treatment system of claim 39, wherein the process gas
25 further includes a hydrofluorocarbon gas.

41. The plasma treatment system of claim 39, wherein the fluorocarbon gas includes at least one fluorocarbon selected from the group consisting of CF₄, C₃F₈, C₄F₆, and C₄F₈.

5 42. The plasma treatment system of claim 41, wherein the carbon-free fluorine gas includes nitrogen trifluoride gas or sulfur hexafluoride gas.

10 43. The plasma treatment system of any one of claims 38 to 42, wherein the process gas further includes a halogen gas component containing a halogen component other than fluorine component.

15 44. A plasma treatment system comprising:
a chamber;
a substrate support provided in the chamber;
a gas supply unit configured to supply a process gas into the chamber, the process gas including a phosphorus gas component, a fluorine gas component, a hydrofluorocarbon gas, and a halogen gas component containing a halogen component other than fluorine component;
20 a plasma generator configured to generate plasma from the process gas; and
a controller configured to control the gas supply unit to supply the process gas into the chamber and control the plasma generator to generate
25 plasma from the process gas in the chamber to etch a silicon-containing film of a substrate supported by the substrate support.

45. The plasma treatment system of claim 44, wherein the fluorine gas component includes at least one component selected from the group consisting of a fluorocarbon gas and a carbon-free fluorine gas.

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46. The plasma treatment system of claim 45, wherein the carbon-free fluorine gas includes nitrogen trifluoride gas or sulfur hexafluoride gas.

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47. The plasma treatment system of any one of claims 43 to 46, wherein the halogen gas component is Cl_2 gas and/or HBr gas.

48. The plasma treatment system of any one of claims 38 to 47, wherein

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the ratio of the flow rate of a second gas to the flow rate of a first gas in the process gas is above 0 and 0.5 or less,

the first gas is all gases included in the process gas excluding the phosphorus gas component, and

the second gas is the phosphorus gas component.

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49. The plasma treatment system of claim 48, wherein the ratio is 0.075 or more and 0.3 or less.

50. The plasma treatment system of any one of claims 38 to 49, wherein

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the substrate support includes a bottom electrode,

the plasma treatment system further comprises a bias power source electrically connected to the bottom electrode,

the bias power source is configured to apply pulsed a bias electric power to the bottom electrode, when the plasma is present in the chamber,
5 and

the bias electric power is a radio-frequency bias electric power or a pulsed DC voltage with negative polarity.

51. The plasma treatment system of claim 50, wherein a frequency
10 defining a period in which the pulsed bias electric power is applied to the bottom electrode is 5 Hz or higher and 100 kHz or lower.

52. The plasma treatment system of one of claims 38 to 51, further comprising a chiller configured to supply a heat exchange medium to a
15 flow channel in a bottom electrode of the substrate support,

wherein the controller is configured to control the chiller to supply the heat exchange medium to the flow channel to set a temperature of the substrate support to 0°C or less before generation of the plasma.

20 53. A plasma treatment system for etching a silicon- silicon-containing film of a substrate having the silicon-containing film and a mask, comprising:

a chamber;

a substrate support provided in the chamber;

25 a gas supply unit configured to supply a process gas into the chamber, the process gas including a hydrogen fluoride gas component,

a phosphorus gas component, and a carbon gas component;

a plasma generator configured to generate plasma from the process gas; and

5 a controller configured to control the gas supply unit to supply the process gas into the chamber and control the plasma generator to generate plasma from the process gas in the chamber to etch a silicon-containing film of the substrate supported by the substrate support.

10 54. The plasma treatment system of claim 53, wherein among the flow rate of the hydrogen fluoride gas component, the flow rate of the phosphorus gas component, and the flow rate of the carbon gas component, the flow rate of the hydrogen fluoride gas component is largest.

15 55. The plasma treatment system of claim 53, wherein the process gas further includes a rare gas, and among the flow rates of all gases in the process gas excluding the rare gas, the flow rate of the hydrogen fluoride gas component is largest.

20 56. The plasma treatment system of any one of claims 53 to 55, further comprising a chiller configured to supply a heat exchange medium to a flow channel in a bottom electrode of the substrate support,

wherein the controller is configured to control the chiller to supply the heat exchange medium to the flow channel to set a temperature of the substrate support to a temperature of 0°C or less or -40°C or less before generation of the plasma.

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57. The plasma treatment system of any one of claims 53 to 56, wherein the process gas further includes a fluorine-free halogen gas component.

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58. The plasma treatment system of any one of claims 38 to 57, wherein the phosphorus gas component includes a halogen component.

59. The plasma treatment system of any one of claims 38 to 57, wherein the phosphorus gas component includes at least one of PF_3 , PCl_3 , PF_5 , PCl_5 , POCl_3 , PH_3 , PBr_3 , or PBr_5 .

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60. The plasma treatment system of any one of claims 38 to 57, wherein the phosphorus gas component includes a fluorine component.

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61. The plasma treatment system of claim 60, wherein the phosphorus gas component includes PF_3 or PF_5 .

62. The plasma treatment system of any one of claims 53 to 57, wherein the carbon gas component includes at least one of fluorocarbon or hydrofluorocarbon.

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63. The plasma treatment system of claim 62, wherein the carbon gas component includes two or more carbon atoms.

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64. The plasma treatment system of any one of claims 38 to 63,

wherein the process gas further includes an oxygen gas component.

65. The plasma treatment system of claim 54, wherein the proportion of the flow rate of the hydrogen fluoride gas component to the flow rate of the process gas excluding a rare gas is 50% or more and less than 99%.

66. The plasma treatment system of claim 53 or 54, wherein the proportion of the flow rate of the phosphorous gas component to the flow rate of the process gas excluding a rare gas is 1% or more and 20% or less.

67. The plasma treatment system of any one of claims 38 to 66, wherein the plasma treatment system is a capacitively coupled plasma treatment system.

68. The plasma treatment system of claim 67, wherein
the plasma generator includes a radio-frequency power source configured to generate a radio-frequency power, and
the radio-frequency power source is configured to supply the radio-frequency power to a bottom electrode of the substrate support to generate the plasma.

69. The plasma treatment system of claim 67, further comprising an upper electrode disposed above the substrate support, wherein
the plasma generator includes a radio-frequency power source configured to generate a radio-frequency power, and

the radio-frequency power source is configured to supply the radio-frequency power to the upper electrode to generate the plasma.

70. The plasma treatment system of claim 68 or 69, wherein a frequency of the radio-frequency power is not less than 27 MHz and not more than 100 MHz.

71. The plasma treatment system of any one of claims 38 to 66, wherein the plasma treatment system is an inductively coupled plasma treatment system.

72. A method of manufacturing a device, comprising etching a silicon-containing film of a substrate by the method of any one of claims 1 to 37.

73. A program performed in a computer of a plasma treatment system to cause the plasma treatment system to perform the method of any one of claims 1 to 37.

74. A recording medium storing the program of claim 73.