## SUMMARY OF THE INVENTION

One embodiment of the invention pertains to a method for developing an organotin resist with a composition comprising a contrast enhancer, wherein said contrast enhancer can be chosen, for example, from a silyl halide, an amide, a sulfonic acid, a carboxylic acid, a thiol, a tin halide, a germanium halide, and mixtures thereof. In some embodiments, the contrast enhancer can be used in combination with gaseous acid halide, HF, HCl, HBr and/or HI, to facilitate reaction. Some water vapor may be desirable in combination with other reactants.

Another embodiment of the invention pertains to a method for developing an organotin resist with a contrast enhancer composition comprising trimethylsilyl halide.

Another embodiment of the invention pertains to a method for developing an organotin resist with a composition comprising an alkyl group.

In another embodiment, the invention pertains to a method for removing material from a patterned substrate after an initial development process wherein the method comprises contacting the patterned substrate to a contrast enhancer in vapor form.

In a first aspect, the invention pertains to a method for enhancing development contrast between irradiated and non-irradiated portions of a radiation sensitive organometallic composition on a substrate surface with a latent image, the method including: contacting the organometallic composition with a reactant gas in an isolated chamber to alter the composition of the irradiated portion, the non-irradiated portion or both, wherein the reactant gas comprises an amide, a sulfonic acid, a diol, a silyl halide, a germanium halide, a tin halide, or mixtures thereof.

In an embodiment of the first aspect, the non-irradiated portions comprise Sn-C bonds.

In an embodiment of the first aspect, the organometallic composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$, wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

In an embodiment of the first aspect, the organometallic composition comprises an oxo-hydroxo network.

In an embodiment of the first aspect, the reactant gas comprises a compound having 1 to 10 carbon atoms.

In an embodiment of the first aspect, the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride, dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

In an embodiment of the first aspect, the reactant gas further comprises water.

In an embodiment of the first aspect, contacting results in breaking of M-O-M and/or M-OH bonds in the organometallic composition.

In an embodiment of the first aspect, contacting results in a release of volatile tin-comprising species from the organometallic composition.

In an embodiment of the first aspect, the non-irradiated portion has an initial thickness and wherein contacting results in the non-irradiated portion having an adjusted thickness, wherein the adjusted thickness is less than the initial thickness.

In an embodiment of the first aspect, the adjusted thickness is no more than 90% of the initial thickness.

In an embodiment of the first aspect, the adjusted thickness is no more than 50% of the initial thickness.

In an embodiment of the first aspect, the non-irradiated portion is essentially completely removed after contacting for no more than 10 minutes to form a developed structure.

An embodiment of the first aspect further includes processing the developed structure to improve the pattern using a liquid rinse and/or a pattern improving reactive gas.

In an embodiment of the first aspect, the pattern improving reactive gas comprises water, a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a hydrogen halide, a germanium halide, a tin halide, an amine, or mixtures thereof.

In an embodiment of the first aspect, the substrate comprises a semiconductor wafer.

In an embodiment of the first aspect, contacting is performed with a reactant gas having a selected flow rate.

In an embodiment of the first aspect, the selected flow rate is from 1 standard cubic centimeters per minute (sccm) to 1000 sccm.

An embodiment of the first aspect further comprises delivering an inert gas to the isolated chamber, wherein the flow rate of the inert gas is from 0.5 standard liters per minute (SLM) to 30 SLM.

In an embodiment of the first aspect, the contacting is performed at a chamber pressure from 100 Torr to 1200 Torr.

In an embodiment of the first aspect, contacting is performed for 3 seconds to 15 minutes.

In an embodiment of the first aspect, contacting is performed at a chamber pressure of 0.001 Torr to 10 Torr.

In an embodiment of the first aspect, the chamber pressure is adjusted by varying the flow rate of gas into the isolated chamber, and wherein the chamber pressure may change over the course of a period of the contacting.

In an embodiment of the first aspect, the substrate, the reactant gas, and/or the isolated chamber are at a temperature from -45°C to 350°C during contacting.

In an embodiment of the first aspect, contacting is performed at a temperature of 100°C to 250°C and at a chamber pressure of at least 0.1 Torr for at least 10 seconds.

In an embodiment of the first aspect, contacting is performed prior to a development process.

In an embodiment of the first aspect, contacting is performed after a development process.

In an embodiment of the first aspect, the development process is a liquid based development process.

In an embodiment of the first aspect, the development process is a dry development process performed with a developing reactive gas or with a plasma.

In an embodiment of the first aspect, the development process formed a negative pattern substantially maintaining an irradiated portion of the organometallic composition.

In an embodiment of the first aspect, the development process formed a positive pattern substantially maintaining an irradiated portion of the organometallic composition.

In an embodiment of the first aspect, contacting is performed with a plurality of reactant gases used simultaneously or in series.

An embodiment of the first aspect further comprises, prior to contacting, heating the organometallic composition at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the organometallic composition for at least 10 minutes.

Disclosed herein is a method for modifying a radiation sensitive organometallic composition on a substrate surface with a latent image formed by respective irradiated and non-irradiated portions, the method includes contacting the organometallic composition with a vapor of a carboxylic acid in an isolation chamber at a partial pressure from 0.1 torr to 50 torr, at a temperature from 100°C to 250°C, with a flow rate from 0.1 sccm to 5000 sccm, at a temperature from -45°C to 250°C to remove a relative amount of the non-irradiated portion ((initial nonirradiated thickness-final non-irradiated thickness)/initial non-irradiated thickness) wherein the relative amount of the non-irradiated portion removed is at least 10%, while a relative amount of thickness of the irradiated portion removed ((initial irradiated thickness-final irradiated thickness)/initial irradiated thickness) is no more than one third of the relative amount of non-irradiated portion removed.

In an embodiment, the non-irradiated portions comprise Sn-C bonds.

In an embodiment, the organometallic composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$, wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

In an embodiment, the carboxylic acid comprises compounds with alkyl chains having 1 to 10 carbon atoms, isomers thereof, halogenated derivatives thereof, and/or amide derivatives of thereof.

In an embodiment, the carboxylic acid comprises formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, benzoic acid, formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, and combinations thereof.

In an embodiment, the carboxylic acid comprises acetic acid.

In an embodiment, the organometallic composition comprises an oxo-hydroxo network.

In an embodiment, contacting results in a release of volatile species from the organometallic composition.

In an embodiment, the method results in removal of from 10% to 90% of the non-irradiated portion.

In an embodiment, the non-irradiated portion is essentially completely removed after contacting the organometallic composition.

In an embodiment, contacting is performed for 10 seconds to 15 minutes and wherein the flow rate is from 1 sccm to 5000 sccm.

In an embodiment, contacting is performed at a chamber pressure from 0.001 Torr to 10 Torr, with a flow rate of at least one gas from 1 to 5000 sccm, for at least 10 seconds.

An embodiment, further comprises, prior to contacting, heating the organometallic composition at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the radiation sensitive organometallic composition for at least 10 minutes.

In a second aspect, the invention pertains to a method for improving the quality of a patterned structure with a negative pattern corresponding to an irradiated organometallic composition on a substrate surface with non-irradiated organometallic composition substantially removed or with a positive pattern corresponding to non-irradiated organometallic composition on a substrate surface with the irradiated organometallic composition substantially removed, the method including: developing a pattern from a latent image formed by irradiating a radiation sensitive organometallic composition on a substrate surface to form a patterned structure; and following completion of the development step, contacting the patterned structure with a reactant gas in an isolated chamber to remove scum from the pattern, wherein the reactant gas is selected from water, a carboxylic acid, an amide, a sulfonic acid, a diol, a silyl halide, a germanium halide, a tin halide, a thiol, a hydrogen halide or mixtures thereof.

In an embodiment of the second aspect, the patterned material comprises Sn-C and/or Sn-O bonds.

In an embodiment of the second aspect, the scum comprises incompletely removed non-irradiated organometallic composition associated with a negative pattern, incompletely removed irradiated organometallic composition associated with a positive pattern, partially irradiated organometallic composition, or mixtures thereof.

In an embodiment of the second aspect, the scum comprises microbridges.

In an embodiment of the second aspect, contacting results in altering the composition of the scum to release of volatile species from the scum.

In an embodiment of the second aspect, the reactant gas comprises compounds having 1 to 10 carbon atoms.

In an embodiment of the second aspect, the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanol, ethanol, n-propanol, iso-propanol, 1-butanol, iso-butanol, tert-butanol, 1-pentanol, 4-methyl-2-pentanol, cyclopentanol, 1-hexanol, cyclohexanol, phenol, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride, dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

In an embodiment of the second aspect, contacting is performed at a temperature of -45°C to 350°C and at a chamber pressure of at least 0.001 Torr for at least 3 seconds.

In an embodiment of the second aspect, contacting is performed with a plurality of reactant gases used simultaneously or in series.

In a third aspect, the invention pertains to a method for dry developing a radiation sensitive organometallic composition having a radiation-patterned latent image on a substrate, the method including: contacting the composition having the latent image with a reactant gas to remove a substantial portion of the non-irradiated regions of the coating, wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises an amide, a sulfonic acid, a diol, a silyl halide, a germanium halide, a tin halide, a thiol, or mixtures thereof.

In an embodiment of the third aspect, the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises a mixture of at least two gases selected from a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, or a thiol.

In an embodiment of the third aspect, the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises a mixture of at least two carboxylic acids, at least two amides, at least two sulfonic acids, at least two alcohols, at least two diols, at least two silyl halides, at least two germanium halides, at least two tin halides, at least two amines, or at least two thiols.

In an embodiment of the third aspect, the composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$,

wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

In an embodiment of the third aspect, the reactant gas comprises compounds having 1 to 10 carbon atoms, optionally substituted with one or more heteroatom functional groups.

In an embodiment of the third aspect, the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanol, ethanol, n-propanol, iso-propanol, 1-butanol, iso-butanol, tert-butanol, 1-pentanol, 4-methyl-2-pentanol, cyclopentanol, 1-hexanol, cyclohexanol, phenol, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride, dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

In an embodiment of the third aspect, the reactant gas further comprises water.

In an embodiment of the third aspect, contacting results in breaking of Sn-O-Sn and/or Sn-OH bonds in the non-irradiated regions of the coating.

In an embodiment of the third aspect, contacting results in a release of volatile species from the composition.

In an embodiment of the third aspect, contacting is performed with a flow rate of the reactant gas from 1 sccm to 5000 sccm.

In an embodiment of the third aspect, contacting is performed for 3 seconds to 15 minutes.

In an embodiment of the third aspect, contacting is performed in an isolated chamber at a pressure of 0.001 Torr to 50 Torr.

In an embodiment of the third aspect, the pressure is adjusted by varying a flow rate of the reactant gas into the isolated chamber.

In an embodiment of the third aspect, contacting is performed at temperature from -45°C to 350°C.

An embodiment of the third aspect further comprises, prior to contacting, heating the organometallic composition at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the organometallic composition for at least 10 minutes.

In a fourth aspect, the invention pertains to a method for developing a radiation sensitive organometallic composition having a radiation-patterned latent image on a substrate, the method including: contacting the radiation patterned material with a first reactant gas composition to modify the non-irradiated regions of the coating, wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the first reactant gas composition comprises a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or a mixture thereof, to form an initial pattern; and, contacting the initial pattern with a second reactant gas composition different from the first reactant gas composition to remove a portion of the initial pattern, wherein the second reactant gas composition comprises a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or a mixture thereof.

In an embodiment of the fourth aspect, contacting the initial pattern with a second reactant gas substantially removes the non-irradiated regions of the coating to form a developed pattern.

An embodiment of the fourth aspect further comprises, prior to contacting the initial pattern with a second reactant gas composition, heating the initial pattern prior at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the initial pattern for at least 10 minutes.

In an embodiment of the fourth aspect, the first and/or second reactant gas further comprises water.

In an embodiment of the fourth aspect, wherein the composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$, wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

In an embodiment of the fourth aspect, contacting with the first and/or second reactant gas results in breaking of Sn-O-Sn and/or Sn-OH bonds in the non-irradiated regions of the coating.

In an embodiment of the fourth aspect, the first and/or second reactant gas comprises a fluorinated carboxylic acid and/or a fluorinated alcohol.

Disclosed herein is an apparatus including: an enclosed chamber; a substrate support within the enclosed chamber, wherein the substrate support is configured to spin a substrate; a gas supply subsystem comprising a gas source reservoir, a gas spray dispenser having a pluralities of openings distributed to provide gas dispensing directed toward a substrate mounted on the substrate support and over the extent of the substrate surface, a gas flow controller, and gas conduits connecting the gas source reservoir and the gas spray dispenser with the flow through the conduits moderated by the gas flow controller; a liquid supply subsystem comprising a liquid reservoir, a nozzle, a nozzle support with a translatable arm for positioning the nozzle, a flow controller and tubing providing flow channels between the liquid reservoir and the nozzle, wherein the nozzle support has a configuration to configure the nozzle to deposit liquid on a substrate mounted on the substrate support; one or more exhausts exiting the chamber; and a pump.

An embodiment further comprises a controller interfaced with a motor of the substrate support to control spinning of the substrate, the gas supply subsystem to control gas flow and liquid supply subsystem to control delivery of liquid from the liquid supply subsystem.

In an embodiment, the gas source reservoir comprises a first reservoir of a first contrast enhancing agent comprising a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or a mixture thereof.

In an embodiment, the gas source reservoir further comprises an inert gas supply.

In an embodiment, the contrast enhancing agent is a liquid in the reservoir and wherein the gas supply subsystem is configured for delivery of the contrast enhancing agent as a vapor through a mass flow controller.

In an embodiment, the gas source reservoir further comprises a second reservoir of a second contrast enhancing agent.

In an embodiment, the liquid reservoir comprises a developing liquid.

In an embodiment, the developing liquid comprises an organic liquid.

In an embodiment, the developing liquid comprises an aqueous liquid.

An embodiment further includes one or more heating elements configured to heat, a substrate, the chamber, a reservoir, flow lines, gas/vapor or combinations thereof.

In an embodiment, the actuator arm can move the nozzle out of the path of flow from the gas spray dispenser.

An embodiment is configured with a pump having sufficient pumping capacity for the gas dispensing subsystem and the liquid dispensing subsystem to operate at pressures from 0.001 Torr to atmospheric pressure.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow chart of latent image processing of a patterned organotin coating via treatment with a contrast enhancer and a dry developer.

Fig. 2 is a flow chart of latent image processing of a patterned organotin coating via treatment with a contrast enhancer after development.

Fig. 3 is a flow chart of latent image processing of a patterned organotin coating using a contrast enhancer as a vapor reactive developer.

Fig. 4 is a schematic view of a process system shown with a vapor delivery system connected to a process chamber.

Fig. 5 is a schematic view of a process system having a showerhead vapor distribution unit.

Fig. 6 is a schematic view of a process system shown with a vapor delivery system and a liquid delivery system connected to a process chamber.

Claims:

1. A method for enhancing development contrast between irradiated and non-irradiated portions of a radiation sensitive organometallic composition on a substrate surface with a latent image, the method comprising:

contacting the organometallic composition with a reactant gas in an isolated chamber to alter the composition of the irradiated portion, the non-irradiated portion or both, wherein the reactant gas comprises an amide, a sulfonic acid, a diol, a silyl halide, a germanium halide, a tin halide, or mixtures thereof.

2. The method of claim 1 wherein the non-irradiated portions comprise Sn-C bonds.

3. The method of claim 1 wherein the organometallic composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$,

wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

4. The method of any one of claims 1-3 wherein the organometallic composition comprises an oxo-hydroxo network.

5. The method of any one of claims 1-4 wherein the reactant gas comprises a compound having 1 to 10 carbon atoms.

6. The method of any one of claims 1-4 wherein the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride,

dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

7. The method of any one of claims 1-6 wherein the reactant gas further comprises water.

8. The method of any one of claims 1-7 wherein contacting results in breaking of M-O-M and/or M-OH bonds in the organometallic composition.

9. The method of any one of claims 1-8 wherein contacting results in a release of volatile tin-comprising species from the organometallic composition.

10. The method of any one of claims 1-9 wherein the non-irradiated portion has an initial thickness and wherein contacting results in the non-irradiated portion having an adjusted thickness, wherein the adjusted thickness is less than the initial thickness.

11. The method of claim 10 wherein the adjusted thickness is no more than 90% of the initial thickness.

12. The method of claim 10 wherein the adjusted thickness is no more than 50% of the initial thickness.

13. The method of any one of claims 1-9 wherein the non-irradiated portion is essentially completely removed after contacting for no more than 10 minutes to form a developed structure.

14. The method of claim 13 further comprising processing the developed structure to improve the pattern using a liquid rinse and/or a pattern improving reactive gas.

15. The method of claim 14 wherein the pattern improving reactive gas comprises water, a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a hydrogen halide, a germanium halide, a tin halide, an amine, or mixtures thereof.

16. The method of any one of claims 1-15 wherein the substrate comprises a semiconductor wafer.

17. The method of any one of claims 1-16 wherein contacting is performed with a reactant gas having a selected flow rate.

18. The method of claim 17 wherein the selected flow rate is from 1 standard cubic centimeters per minute (sccm) to 1000 sccm.

19. The method of claim 18 further comprising delivering an inert gas to the isolated chamber, wherein the flow rate of the inert gas is from 0.5 standard liters per minute (SLM) to 30 SLM.

20. The method of claim 19 wherein the contacting is performed at a chamber pressure from 100 Torr to 1200 Torr.

21. The method of any one of claims 1-20 wherein contacting is performed for 3 seconds to 15 minutes.

22. The method of any one of claims 1-19 or 21 wherein contacting is performed at a chamber pressure of 0.001 Torr to 10 Torr.

23. The method of any one of claims 1-22 wherein the chamber pressure is adjusted by varying the flow rate of gas into the isolated chamber, and wherein the chamber pressure may change over the course of a period of the contacting.

24. The method of any one of claims 1-23 wherein the substrate, the reactant gas, and/or the isolated chamber are at a temperature from -45°C to 350°C during contacting.

25. The method of any one of claims 1-23 wherein contacting is performed at a temperature of 100°C to 250°C and at a chamber pressure of at least 0.1 Torr for at least 10 seconds.

26. The method of any one of claims 1-12 and 16-26 wherein contacting is performed prior to a development process.

27. The method of any one of claims 1-12 and 16-26 wherein contacting is performed after a development process.

28. The method of claim 27 wherein the development process is a liquid based development process.

29. The method of claim 27 wherein the development process is a dry development process performed with a developing reactive gas or with a plasma.

30. The method of any one of claims 27-29 wherein the development process formed a negative pattern substantially maintaining an irradiated portion of the organometallic composition.

31. The method of any one of claims 27-29 wherein the development process formed a positive pattern substantially maintaining an irradiated portion of the organometallic composition.

32. The method of any one of claims 1-31 wherein contacting is performed with a plurality of reactant gases used simultaneously or in series.

33. The method of any one of claims 1-32 further comprising, prior to contacting, heating the organometallic composition at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the organometallic composition for at least 10 minutes.

34. The method of any one of claims 1-33 wherein, after contacting, an altered non-irradiated portion of the organometallic composition, an altered irradiated portion of the organometallic composition or both is on the substrate surface.

35. A method for improving the quality of a patterned structure with a negative pattern corresponding to an irradiated organometallic composition on a substrate surface with non-

irradiated organometallic composition substantially removed or with a positive pattern corresponding to non-irradiated organometallic composition on a substrate surface with the irradiated organometallic composition substantially removed, the method comprising:

developing a pattern from a latent image formed by irradiating a radiation sensitive organometallic composition on a substrate surface to form a patterned structure; and

following completion of the development step, contacting the patterned structure with a reactant gas in an isolated chamber to remove scum from the pattern, wherein the reactant gas is selected from water, a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an alkyl amine, a thiol, a hydrogen halide or mixtures thereof.

36. The method of claim 35 wherein the patterned material comprises Sn-C and/or Sn-O bonds.

37. The method of claim 35 or claim 36 wherein the scum comprises incompletely removed non-irradiated organometallic composition associated with a negative pattern, incompletely removed irradiated organometallic composition associated with a positive pattern, partially irradiated organometallic composition, or mixtures thereof.

38. The method of any one of claims 35-37 wherein the scum comprises microbridges.

39. The method of any one of claims 35-38 wherein contacting results in altering the composition of the scum to release of volatile species from the scum.

40. The method of any one of claims 35-39 wherein the reactant gas comprises compounds having 1 to 10 carbon atoms.

41. The method of any one of claims 35-40 wherein the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanol, ethanol, n-propanol, iso-propanol, 1-butanol, iso-butanol, tert-butanol, 1-pentanol, 4-methyl-2-pentanol, cyclopentanol, 1-hexanol, cyclohexanol, phenol, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol,

ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride, dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

42. The method of any one of claims 35-41 wherein contacting is performed at a temperature of -45°C to 350°C and at a chamber pressure of at least 0.001 Torr for at least 3 seconds.

43. The method of any one of claims 35-42 wherein contacting is performed with a plurality of reactant gases used simultaneously or in series.

44. A method for dry developing a radiation sensitive organometallic composition having a radiation-patterned latent image on a substrate, the method comprising:

contacting the composition having the latent image with a reactant gas to remove a substantial portion of the non-irradiated regions of the coating, wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or mixtures thereof.

5745. The method of claim 44 wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises a mixture of at least two gases selected from a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, or a thiol.

46. The method of claim 44 wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the reactant gas comprises a mixture of at least two carboxylic acids, at least two amides, at least two sulfonic acids, at least two alcohols, at least two diols, at least two silyl halides, at least two germanium halides, at least two tin halides, at least two amines, or at least two thiols.

47. The method of any one of claims 44-46 wherein the composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$,

wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

48. The method of any one of claims 44-47 wherein the reactant gas comprises compounds having 1 to 10 carbon atoms, optionally substituted with one or more heteroatom functional groups.

49. The method of any one of claims 44-47 wherein the reactant gas comprises formamide, N-methylformamide, acetamide, urea, propanamide, butyramide, isobutyramide, methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanol, ethanol, n-propanol, iso-propanol, 1-butanol, iso-butanol, tert-butanol, 1-pentanol, 4-methyl-2-pentanol, cyclopentanol, 1-hexanol, cyclohexanol, phenol, methanethiol, ethanethiol, propanethiol, isopropanethiol, butyrothiol, isobutyrothiol, tert-butylthiol, methylene glycol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, cyclohexanediol, trimethylsilyl chloride, trimethylsilyl bromide, dimethylsilyl chloride, dimethylsilyl bromide, monomethylsilyl chloride, monomethylsilyl bromide, tetrachlorosilane, tetrabromosilane, and combinations thereof.

50. The method of any one of claims 44-49 wherein the reactant gas further comprises water.

51. The method of any one of claims 44-50 wherein contacting results in breaking of Sn-O-Sn and/or Sn-OH bonds in the non-irradiated regions of the coating.

52. The method of any one of claims 44-51 wherein contacting results in a release of volatile species from the composition.

53. The method of any one of claims 44-52 wherein contacting is performed with a flow rate of the reactant gas from 1 sccm to 5000 sccm.

54. The method of any one of claims 44-53 wherein contacting is performed for 3 seconds to 15 minutes.

55. The method of any one of claims 44-54 wherein contacting is performed in an isolated chamber at a pressure of 0.001 Torr to 50 Torr.

56. The method of claim 55 wherein the pressure is adjusted by varying a flow rate of the reactant gas into the isolated chamber.

57. The method of claim 55 or claim 56 wherein contacting is performed at temperature from -45°C to 350°C.

58. The method of claim 55 or claim 56 further comprising, prior to contacting, heating the organometallic composition at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the organometallic composition for at least 10 minutes.

59. A method for developing a radiation sensitive organometallic composition having a radiation-patterned latent image on a substrate, the method comprising:

contacting the radiation patterned material with a first reactant gas composition to modify the non-irradiated regions of the coating, wherein the non-irradiated regions of the coating comprise Sn-C bonds, and the first reactant gas composition comprises a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or a mixture thereof, to form an initial pattern; and,

contacting the initial pattern with a second reactant gas composition different from the first reactant gas composition to remove a portion of the initial pattern, wherein the second reactant gas composition comprises a carboxylic acid, an amide, a sulfonic acid, an alcohol, a diol, a silyl halide, a germanium halide, a tin halide, an amine, a thiol, or a mixture thereof.

60. The method of claim 59 wherein contacting the initial pattern with a second reactant gas substantially removes the non-irradiated regions of the coating to form a developed pattern.

61. The method of claim 59 or claim 60 further comprising, prior to contacting the initial pattern with a second reactant gas composition, heating the initial pattern prior at a temperature of 45°C to 300°C for at least 0.1 minutes and/or aging the initial pattern for at least 10 minutes.

62. The method of any one of claims 59-61 wherein the first and/or second reactant gas further comprises water.

63. The method of any one of claims 59-62 wherein the composition comprises a composition represented by the formula $R_zSnO_{(2-z/2-x/2)}(OH)_x$, where $0 < x < 3$, $0 < z \leq 2$, $x + z \leq 4$,

wherein R is a hydrocarbyl or organo group with 1-31 carbon atoms, with a carbon atom bonded to Sn and with one or more carbon atoms optionally substituted with one or more heteroatom functional groups.

64. The method of claim 63 wherein contacting with the first and/or second reactant gas results in breaking of Sn-O-Sn and/or Sn-OH bonds in the non-irradiated regions of the coating.

65. The method of any one of claims 59-64 wherein the first and/or second reactant gas comprises a fluorinated carboxylic acid and/or a fluorinated alcohol.