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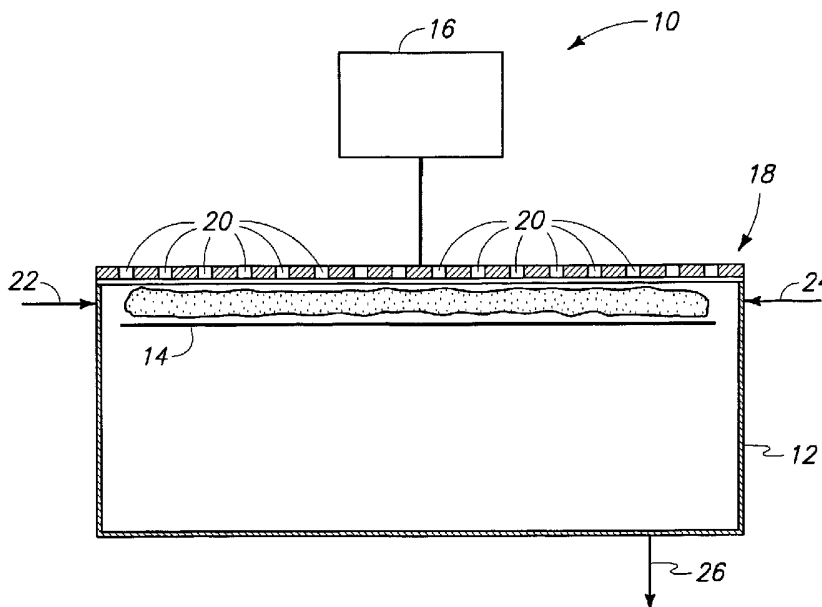
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(54) Title: ATOMIC LAYER DEPOSITION METHODS



(57) Abstract: A first precursor gas is flowed to the substrate within the chamber effective to form a first monolayer on the substrate. A second precursor gas different in composition from the first precursor gas is flowed to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with the first monolayer and form a second monolayer on the substrate which is different in composition from the first monolayer. The second monolayer includes components of the first monolayer and the second precursor. In one implementation, the first and second precursor flowings are successively repeated effective to form a mass of material on the substrate of the second monolayer composition. Additional and other implementations are contemplated.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION**ATOMIC LAYER DEPOSITION METHODS****Technical Field**

5 This invention relates to atomic layer deposition methods.

Background Art

Semiconductor processing in the fabrication of integrated circuitry typically includes the deposition of layers on semiconductor substrates. One such method is atomic layer deposition (ALD), which involves the deposition of successive monolayers
10 over a substrate within a deposition chamber typically maintained at subatmospheric pressure. With typical ALD, successive monoatomic layers are adsorbed to a substrate and/or reacted with the outer layer on the substrate, typically by the successive feeding of different deposition precursors to the substrate surface.

An exemplary ALD method includes feeding a single vaporized precursor to a
15 deposition chamber effective to form a first monolayer over a substrate received therein. Thereafter, the flow of the first deposition precursor is ceased and an inert purge gas is flowed through the chamber effective to remove any remaining first precursor which is not adhering to the substrate from the chamber. Subsequently, a second vapor
20 deposition precursor, different from the first, is flowed to the chamber effective to form a second monolayer on/with the first monolayer. The second monolayer might react with the first monolayer. Additional precursors can form successive monolayers, or the above process can be repeated until a desired thickness and composition layer has been formed over the substrate.

Summary

25 The invention comprises atomic layer deposition methods. In one implementation, a semiconductor substrate is positioned within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the chamber effective to form a first monolayer on the substrate. A second precursor gas different in
30 composition from the first precursor gas is flowed to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with the first monolayer and form a second monolayer on the substrate which is different in composition from the first monolayer. The second monolayer includes components of the first monolayer and the second precursor. In one implementation, the first and second precursor flowings are successively repeated effective to form a
35 mass of material on the substrate of the second monolayer composition. In one implementation, after the second precursor gas flowing, a third precursor gas different

in composition from the first and second precursor gases is flowed to the second monolayer within the chamber effective to react with the second monolayer and form a third monolayer on the substrate which is different in composition from the first and second monolayers. In one implementation, after the second precursor gas flowing, the first precursor gas is flowed to the substrate within the chamber effective to react with the second monolayer and both a) remove a component of the second monolayer to form a third composition monolayer on the substrate which is different in composition from the first and second monolayers; and b) form a fourth monolayer of the first monolayer composition on the third composition monolayer.

Other aspects and implementations not necessarily generic to any of the above are contemplated and disclosed.

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 sectional view of an exemplary atomic layer deposition apparatus usable in accordance with an aspect of the invention.

Fig. 2 is a series of diagrammatic molecular level views of an exemplary method in accordance with an aspect of the invention.

Fig. 3 is a series of diagrammatic molecular level views of an exemplary method in accordance with an aspect of the invention.

Fig. 4 is a series of diagrammatic molecular level views of an exemplary method in accordance with an aspect of the invention.

Fig. 5 is a series of common timelines showing exemplary gas flows and power levels of processing in accordance with exemplary aspects of the invention.

Fig. 6 is an alternate series of common timelines to that depicted by Fig. 5.

Fig. 7 is another alternate series of common timelines to that depicted by Fig. 5.

Fig. 8 is still another alternate series of common timelines to that depicted by Fig. 5.

Fig. 9 is yet another alternate series of common timelines to that depicted by Fig. 5.

Fig. 10 is another alternate series of common timelines to that depicted by Fig. 5.

Best Modes for Carrying Out the Invention and Disclosure of Invention

Fig. 1 depicts an exemplary atomic layer deposition apparatus usable in accordance with an aspect of the invention. Such an apparatus enables the generation of a surface microwave plasma within a chamber within which atomic layer deposition

is conducted relative to a semiconductor substrate. In the context of this document, "surface microwave plasma" is defined as a plasma generated in a gas against a substrate being processed by transmitting microwave energy from a plurality of discrete, spaced microwave emitting sources, and whether conducted in existing or
5 yet-to-be-developed manners. One existing manner of doing so is by use of an antenna, such as a surface plane antenna (SPA) or a radial line slot antenna (RLSA). By way of example only, examples can be found in U.S. Patent Nos. 6,399,520 and 6,343,565, which are hereby incorporated by reference herein.

Apparatus 10 is diagrammatically depicted as comprising a deposition chamber 12
10 having a semiconductor substrate 14 positioned therein. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" 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
15 in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above. A suitable support or mechanism (not shown) can be provided for supporting substrate 14 therein, and which might be temperature controlled, powered and/or otherwise configured for positioning a substrate 14 within chamber 12 as desired.

20 A suitable microwave generator 16 is operatively connected with a surface plane antenna 18 received just above deposition chamber 12. Typically, surface plane antenna 18 is comprised of a metal material having a plurality of microwave transmissive openings 20 formed therein through which microwave energy generated by source 16 passes to within chamber 12, and proximate the surface of substrate 14. The
25 upper wall of chamber 12 over which surface plane antenna 18 is received is also, therefore, provided to be microwave transmissive. Of course, some or all of surface plane antenna 18 could be provided within deposition chamber 12. An exemplary preferred spacing from the upper surface of substrate 13 to the lower surface of second antenna 28 is 65mm. Of course, greater or small spacings can be utilized. In certain
30 situations, spacings considerably less than 65mm might be utilized. Further, in addition to microwave, energy generation is also contemplated in combination with microwave energy generation, and whether within or externally of chamber 12.

Exemplary precursor and/or purge gas inlets 22 and 24 are shown diagrammatically for emitting precursor and/or purge gases to within chamber 12
35 intermediate substrate 14 and surface plane antenna 18. A vacuum draw-down line 26 is diagrammatically shown for exhausting material from chamber 26. The Fig. 1

apparatus is diagrammatic and exemplary in construction only, with any other suitable apparatus being usable in accordance with the methodical aspects of the invention. For example, any alternate configuration, such as showerheads, multiple ports or other means, whether existing or yet-to-be developed, are also of course contemplated for getting gas
5 to the chamber and exhausting material from the chamber.

A semiconductor substrate, such as substrate 14, is positioned within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the chamber, for example through one or both of inlets 22 and 24, effective to form a first monolayer on the substrate. By way of example only, and with respect to forming an
10 exemplary TiB_2 layer, an exemplary first precursor gas includes $TiCl_4$, and, for example, alone or in combination with inert or other gases. An exemplary first monolayer produced from such $TiCl_4$ is $TiCl_x$, for example as depicted relative to Fig. 2. Fig. 2 illustrates exemplary sequential processing in an atomic layer deposition method utilizing $TiCl_4$. The far left illustrated portion of Fig. 2 depicts a suitable substrate surface 30
15 having a first monolayer 32 comprising $TiCl_x$ adhered thereto. Such, by way of example only, is in the form of titanium adhering to substrate surface 30 with chlorine atoms or molecules extending outwardly from the titanium.

Typically, any remaining first precursor gas would then be purged from the chamber using an inert purge gas, or by some other method. Regardless, a second
20 precursor gas, different in composition from the first precursor gas, is then flowed to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with the first monolayer and form a second monolayer on the substrate which is different in composition from the first monolayer, with the second monolayer comprising components of the first monolayer and the second
25 precursor. In the context of this document, a gas being "different in composition" means some gas having an alternate and/or additional reactive component from the gas to which it is being compared.

The middle view in Fig. 2 depicts an exemplary preferred second precursor gas as comprising B_2H_6 and in an activated state under surface microwave plasma conditions.
30 As depicted in the far right view, such is effective to react with first monolayer 32 to form a second monolayer 34 which comprises TiB_2 , with HCl as a by-product. Second monolayer 34 comprises a component of the first monolayer (i.e., Ti) and a component of the second precursor (i.e., B).

The above described first and second precursor flowings are successively repeated
35 effective to form a mass of material on the substrate of the second monolayer composition. The fabricated mass might comprise, consist essentially of, or consist of

the second monolayer composition. For example, the invention contemplates the possibility of fabricating the mass to include materials other than solely the second monolayer composition, for example by introducing alternate first and/or second precursor gases as compared to only using the above-described first and second precursor gases in forming the mass of material on the substrate.

The exemplary above-described process has the second monolayer component from the first monolayer as being a metal in elemental form (i.e., titanium), wherein the second monolayer comprises a conductive metal compound. Further in one preferred embodiment, the mass of material is formed to be conductive. By way of example only, an alternate of such processing would be to utilize a first precursor gas comprising $TaCl_5$ to form a first monolayer comprising $TaCl_x$. In such instance, an exemplary second precursor gas comprises NH_3 to form a second monolayer comprising TaN . As with the first-described embodiment, inert gases, flow rates, power, temperature, pressure and any other operating parameter can be selected and optimized by the artisan, with no particular one or set of parameters being preferred in the context of the invention.

Alternately by way of example only, the second monolayer could be formed to comprise a dielectric material, and further by way of example only, the mass of material fabricated to be insulative. For example for forming an insulative mass comprising Al_2O_3 , exemplary gases include trimethylaluminum as a first precursor gas, and O_3 and/or H_2O as a second precursor gas.

Also in any of the above-described and subsequent embodiments, the first precursor gas flowing can be with or without plasma within the chamber, for example with or without surface microwave plasma generation within the chamber with the first precursor gas flowing. Further, remote plasma generation could also be utilized with the first precursor gas flowing, and also with the second precursor gas flowing in combination with surface microwave plasma conditions within the chamber during the second precursor gas flowing.

In one implementation, an atomic layer deposition method includes the above generically described first and second precursor gas flowings. After the second precursor gas flowing, a third precursor gas different in composition from the first and second precursor gases is flowed to the second monolayer within the chamber effective to react with the second monolayer and form a third monolayer on the substrate which is different in composition from the first and second monolayer. The first, second and third precursor flowings can be successively repeated effective to form a mass of material on the substrate which comprises, consists essentially of or consists of the third monolayer composition. By way of example only in accordance with this

implementation, exemplary processing is further described with reference to Fig. 3 in the formation of a third monolayer comprising an aluminum oxide.

Specifically, the far left illustrated view of Fig. 3 depicts the result of flowing a first precursor gas comprising trimethylaluminum to form a first monolayer 40 comprising AlCH_x onto a substrate surface 30. A second precursor gas, for example H_2 , is flowed to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with first monolayer 40 and form a different composition second monolayer 42 on the substrate. Illustrated second monolayer 42 comprises a component from first monolayer 40 (Al) and a component from the second precursor (H). A third precursor gas (i.e., O_3 and/or H_2O) is flowed to second monolayer 42 within the chamber effective to react therewith and form a third monolayer 44 (i.e., AlO_x) on substrate 30 which is different in composition from first monolayer 40 and second monolayer 42. Of course, such processing can be repeated to deposit a desired thickness aluminum oxide comprising layer by atomic layer deposition. Further of course, one, both or neither of the first and third precursor gas flowings could comprise remote and/or chamber generated plasma, and for example include surface microwave plasma conditions.

By way of example only and where a desired finished product is TiN, an exemplary alternate first precursor gas is TiCl_4 to form a monolayer comprising TiCl_x . An exemplary second precursor gas could still comprise H_2 , with an exemplary third precursor gas comprising NH_3 . Further by way of example, another deposited material is TaN as the third monolayer. An exemplary first precursor gas is TaCl_5 to form the first monolayer to comprise TaCl_x . An exemplary second precursor gas is H_2 and an exemplary third precursor gas is NH_3 .

In one implementation, processing occurs as described above generically with respect to the first and second precursor gas flowings. After the second precursor gas flowing, the first precursor gas is flowed to the substrate within the chamber effective to react with the second monolayer and both a) remove a component of the second monolayer to form a third composition monolayer on the substrate which is different in composition from the first and second monolayers, and b) form a fourth monolayer of the first monolayer composition on the third composition monolayer. By way of example only, exemplary processing is more specifically described in Fig. 4 in connection with the fabrication of an elemental tantalum layer.

The far left illustrated view of Fig. 4 depicts processing after flowing a first precursor gas comprising TaCl_5 to form a first monolayer 60 comprising TaCl_x onto a substrate surface 30. This is followed by flowing a second precursor gas (i.e., H_2)

which is different in composition from the first precursor gas to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with the first monolayer to form a second monolayer 62 on the substrate which is different in composition from the first monolayer. Second monolayer 62 comprises a component of the first monolayer (i.e., Ta) and a component of the second precursor (i.e., H). Subsequently, the first precursor gas (i.e., TaCl₅) is flowed to the substrate within the chamber effective to react with second monolayer 62 to both a) remove a component of the second monolayer (i.e., H) to form a third composition monolayer 64 (i.e., Ta), which is different in composition from first monolayer 60 and second monolayer 62, and b) form a fourth monolayer 66 (i.e., TaCl_x) of the first monolayer composition on third composition monolayer 64. Such can be successively repeated to form a mass of material on the substrate comprising, consisting essentially of, or consisting of the third composition monolayer. Again, the first and third precursor flowings can be with or without plasma within the chamber, for example with or without surface microwave plasma.

The depicted and preferred Fig. 4 processing forms the third composition monolayer to comprise a metal in elemental form. By way of example only, alternate exemplary processing for the fabrication of a titanium layer might utilize a first precursor gas comprising TiCl₄ to form the first monolayer to comprise TiCl_x. In such instance, a preferred exemplary second precursor again comprises H₂.

The invention has particular advantageous utility where the first monolayer is of a composition which is substantially unreactive with the second precursor under otherwise identical processing conditions but for presence of surface microwave plasma within the chamber. First monolayers as described above with reference to Figs. 2-4 can constitute such compositions.

At least with respect to a second precursor gas flowing which is different from the first to form the first monolayer within the chamber under surface microwave plasma conditions, the various above-described processings can provide better uniformity and utilize lower ion energy in facilitating an atomic layer deposition which is plasma enhanced in comparison to higher ion energy plasmas which are not expected to provide as desirable a uniformity.

The above-described processings can occur in any manner as literally stated, for example with or without intervening inert purge gas flowings and under any existing or yet-to-be developed processing parameters. Further by way of example only, the openings within the antenna might be made to be gas transmissive as well as microwave transmissive and the antenna provided with the chamber. In such instance, gas might

be flowed through the plurality of openings while transmitting microwave energy through the plurality of openings to the processing chamber effective to form a surface microwave plasma onto a substrate received within the processing chamber. Gas inlets could be configured to flow first to the antennas, and then into the chamber through the
5 openings with the microwave energy which is transmitted through the same openings, or through different openings. Such processing can be void of flowing any gas to the chamber during transmitting of the microwave energy other than through the plurality of openings, if desired.

Further by way of example only, exemplary preferred processing for carrying out
10 the above exemplary methods is described below in conjunction with TiCl_4 as a first precursor gas and H_2 as a second precursor gas, and utilizing an inert purge gas comprising helium. The below-described preferred embodiments/best modes disclosure for practicing exemplary methods as described above are also considered to constitute independent inventions to those described above, and as are more specifically and
15 separately claimed.

Referring generally to Figs. 5-9, such essentially depict a common horizontal timeline showing different respective gas pulses separately broken out in the form of a first precursor gas (i.e., TiCl_4), an inert purge gas (i.e., He), and a second precursor gas (i.e., H_2). The H_2 timeline also has associated therewith dashed lines intended to depict
20 the application of energy at least the elevated-most surfaces of which are intended to depict a power level effective to form a plasma of the exemplary H_2 gas flowing within the chamber. Such might, and preferably does, constitute surface microwave plasma generation within a suitable chamber, for example as described above in connection with the first above embodiments, although is not so limited with respect to the Figs. 5-9
25 embodiments unless found literally in a claim under analysis.

Referring initially to Fig. 5, a semiconductor substrate would be positioned within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the chamber effective to form a first monolayer on the substrate, for example as depicted by a TiCl_4 gas pulse P1. Plasma generation might or might not be utilized.
30 After flowing the first monolayer, an inert purge gas is flowed to the chamber, for example as depicted by a helium gas pulse P2. After flowing the inert purge gas, a second precursor gas is flowed to the substrate under plasma conditions within the chamber effective to form a second monolayer on the substrate which is different in composition from the first monolayer, for example as depicted by an H_2 gas pulse P3.
35 The second precursor gas is different in composition from the first precursor gas.

The plasma conditions within the chamber comprise the application of energy to the chamber at some power level 40 capable of sustaining plasma conditions within the chamber with the second precursor gas P3. The application of such energy to the chamber commences along an increasing power level 42 up to plasma capable power level 40 at a time point 44 prior to flowing the second precursor gas to the chamber, for example as depicted at time point 45. In the exemplary depicted Fig. 5 embodiment, the power level increasing along line 42 is continuous, and also preferably at a substantially constant rate. The first monolayer might be formed in the presence or absence of plasma within the chamber. Further in one preferred embodiment in connection with Figs. 5-9, and for example as described in the initial embodiments, the second monolayer formed may result from a reaction with the first monolayer, with the second monolayer comprising components of the first monolayer and the second precursor. Further in the exemplary Fig. 5 depicted embodiment, inert purge gas flowing P2 and second precursor gas flowing P3 do not overlap. By way of example only, exemplary time periods for all pulses is one second. Although of course, greater, less and/or unequal times could be utilized.

After forming the second monolayer, another inert purge gas flowing P4 (the same or different in composition in some way to that of the first precursor gas) is begun prior to commencing a reducing of the plasma capable power. For example, Fig. 5 depicts the P4 pulse commencing at a time point 46 which is before a time point 48 when a reducing from the plasma capable power starts to occur.

In the depicted Fig. 5 embodiment, and by way of example only, second precursor pulse P3 and the other inert purge gas pulse P4 do not overlap. Further, the second precursor gas flowing to the chamber is ceased prior to commencing a reducing of the plasma capable power. By way of example, such is depicted at a time point 50, where the second precursor gas flow is ceased, in comparison with later-in-time point 48 where power begins to reduce from power level 40. The above exemplary processing can be repeated, of course, for example as shown by gas pulses P5, P6 and P7.

Another exemplary embodiment is described with reference to Fig. 6. As with the Fig. 5 embodiment, a semiconductor substrate is positioned within an atomic layer deposition chamber and a first precursor gas is flowed to the substrate within the chamber effective to form a first monolayer on the substrate. Such is depicted by the exemplary P1 TiCl_4 pulsing. After forming the first monolayer, a second precursor gas is flowed to the substrate under plasma conditions within the chamber effective to form a second monolayer on the substrate which is different in composition from the first monolayer. The second precursor gas is different in composition from the first precursor

gas, and is depicted by P3 as an example only with respect to an exemplary H₂ second precursor gas flowing.

In Fig. 6, plasma generation of the second precursor gas within the chamber occurs from a second applied power level of energy 40 to the chamber which is capable
5 of generating plasma within the chamber. Some steady-state, first-applied power level of such energy is applied to the chamber at some point prior at least prior to applying the second-applied power level of such energy 40. An exemplary steady-state, first-applied power level 62 is depicted in Fig. 6 which is less than second-applied power level 40, with an increasing from first-applied power 62 to second-applied power
10 level 40 occurring along a line 64.

In one preferred embodiment, steady-state first power 62 is insufficient to generate plasma from the flowing second precursor gas. In one preferred embodiment, steady-state first power 62 is insufficient to generate plasma from the flowing first precursor gas. In the depicted exemplary preferred Fig. 6 embodiment, steady-state first
15 power 62 is applied during first precursor flowing P1, and under conditions effective to form a first monolayer on the substrate under non-plasma conditions within the chamber. In one embodiment, first power level 62 can be considered as a base power level of energy.

Fig. 6 also depicts a purge gas flowing P2 to the chamber intermediate first
20 precursor gas flowing P1 and second precursor gas flowing P2, with steady-state first power 62 being applied during purge gas flowing P2. Further, base power level 62 is raised to power level 40 during a portion of inert purge gas flowing P2.

In the preferred Fig. 6 embodiment, a purge gas flowing P4 occurs after the second precursor gas flowing P3, with a return to power level 62 occurring during such
25 purge gas flowing P4 and after a ceasing of flow of second precursor gas P3. The exemplary processing is depicted as being repeated in connection with gas pulses P5, P6 and P7, and provides but one example of depositing one or more additional monolayers onto the second monolayer. Fig. 6 depicts commencing the raising or increasing of the power level at a point in time 66 which is prior to a point in time 68
30 when second precursor gas flowing P3 begins. Further in the preferred Fig. 6 embodiment, reducing from power level 40 is commenced at a time point 70 which occurs after a time point 72 where second precursor gas pulse P3 flow is ceased.

By way of example only, Figs. 5 and 6 illustrate exemplary preferred
embodiments wherein the respective gas pulses in no way overlap. The invention also
35 contemplates at least some overlapping of the gas pulses, of course. By way of

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example only, and particularly with reference to the second precursor gas pulsing, exemplary overlappings are described with reference to Figs. 7-10.

Referring initially to Fig. 7, such is the same as Fig. 6 except the inert P2 pulse is extended to continue over the P3 pulse, with the inert P2 pulse flowing ceasing after
5 a ceasing of second precursor gas flowing P3.

Referring to Fig. 8, a first precursor gas is flowed to the substrate within an atomic layer deposition chamber effective to form a first monolayer on the substrate, for example as depicted with respect to TiCl_4 with a gas pulse P1. After forming the first monolayer, an inert purge gas is flowed to the chamber, for example as designated by
10 helium gas pulse P2. After flowing the inert purge gas, a second precursor gas is flowed to the substrate under plasma conditions within the chamber effective to form a second monolayer on the substrate which is different in composition from the first monolayer. In some manner, the second precursor gas is different in composition from the first precursor gas, for example as depicted in Fig. 8 by H_2 pulse P3.

As also depicted in Fig. 8, the second precursor gas flowing under plasma
15 conditions within the chamber commences at an exemplary time point 76 before a time point 77 when inert purge gas flow P2 is ceased. Further, inert purge gas flow P2 ceases at the exemplary time point 77 after the commencing and while the second precursor gas flowing under plasma conditions within the chamber is occurring. Further,
20 Fig. 8 depicts that the plasma conditions within the chamber comprise the application of energy to the chamber at a power level 40 which is capable of sustaining plasma conditions within the chamber with the second precursor gas. Fig. 8 also depicts a minimum application of a base power level 62, and a raising therefrom to power level 40 along a segment 78. However also with respect to the Fig. 8 exemplary
25 embodiment, an aspect of the invention contemplates zero power being applied as opposed to some base level 62. Regardless and in a non-limiting fashion, Fig. 8 also depicts second precursor gas pulse P3 commencing at a time point 80 and the power level increasing along line 78 commencing at a time point 82 which is after time point 80.

After forming the second monolayer, another inert purge gas flow P4 is depicted
30 as commencing at a point in time 84 which is prior to a point in time 86 when the second precursor gas flow is ceased. Of course, such processing can be repeated for example as depicted by gas pulses P5, P6 and P7.

By way of example only, Fig. 9 depicts an alternate embodiment whereby the
35 commencing of an application of energy to the chamber at the increasing power level up to a plasma capable power level 40 occurs commensurate with point in time 80

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constituting the beginning of the flow of the second precursor gas to the chamber. Also by way of example only, Fig. 8 depicts power levels starting from and returning to zero, with the arrival at zero power also occurring at time point 86 when the flow of the second precursor is ceased.

5 Further by way of example only, Fig. 10 depicts a process whereby the application of energy to the chamber at the increasing power level up to power level 40 commences at a time point 90 which is prior to time point 80 when the flow of the second precursor gas to the chamber commences.

By way of example only, plasmas generated from microwaves are typically
10 characterized by a very shallow skin depth, with the power being very effectively consumed in a very small volume. Surface microwave plasma typically results from generation of uniform plasma from microwave by means of distributing or spreading out the microwave energy prior to entry into the reaction chamber. The microwave power is typically converted from a waveguide transmission mode into waves that run parallel
15 to an upper reactor plane antenna/window. This conversion to surface wave is produced by a diverting antenna that acts to reflect the microwaves. Once the microwaves are running parallel to the upper plane antenna, small openings in the plane antenna allow portions of the microwave to be released to the reaction chamber thus spreading the power over the desired area. The periodicity of the openings in the plane antenna
20 determine the locality and uniformity of the power spread.

CLAIMS

1. An atomic layer deposition method comprising:
positioning a semiconductor substrate within an atomic layer deposition chamber;
5 flowing a first precursor gas to the substrate within the chamber effective to form a first monolayer on the substrate;
flowing a second precursor gas different in composition from the first precursor gas to the first monolayer within the chamber under surface microwave plasma conditions within the chamber effective to react with the first monolayer and form a
10 second monolayer on the substrate which is different in composition from the first monolayer, the second monolayer comprising components of the first monolayer and the second precursor; and
successively repeating said first and second precursor flowings effective to form a mass of material on the substrate of the second monolayer composition.
15
2. The method of claim 1 wherein the first precursor gas comprises TiCl_4 and the first monolayer comprises TiCl_x .
3. The method of claim 1 wherein the first precursor gas comprises TiCl_4 ,
20 the first monolayer comprises TiCl_x , the second precursor gas comprises B_2H_6 , and the second monolayer comprises TiB_2 .
4. The method of claim 1 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , the second precursor gas comprises B_2H_6 , the
25 second monolayer comprises, and the mass is formed to consist essentially of TiB_2 .
5. The method of claim 1 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , the second precursor gas comprises B_2H_6 , the second monolayer comprises TiB_2 , and the mass is formed to consist of TiB_2 .
30
6. The method of claim 1 wherein the first precursor gas flowing is void of plasma within the chamber.
7. The method of claim 1 wherein the first precursor gas flowing is void
35 of surface microwave plasma within the chamber.

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8. The method of claim 1 wherein the first precursor gas flowing comprises plasma within the chamber.

9. The method of claim 1 wherein the first precursor gas flowing comprises
5 surface microwave plasma within the chamber.

10. The method of claim 1 wherein the first monolayer is of a composition which is substantially unreactive with the second precursor under otherwise identical processing conditions but for presence of surface microwave plasma within the chamber.

10

11. The method of claim 1 wherein the first precursor gas comprises TaCl_5 and the first monolayer comprises TaCl_x .

12. The method of claim 1 wherein the first precursor gas comprises TaCl_5 ,
15 the first monolayer comprises TaCl_x , the second precursor gas comprises NH_3 , and the second monolayer comprises TaN .

13. The method of claim 1 wherein the first precursor gas comprises TaCl_5 ,
the first monolayer comprises TaCl_x , the second precursor gas comprises NH_3 , the second
20 monolayer comprises TaN , and the mass is formed to consist essentially of TaN .

14. The method of claim 1 wherein the first precursor gas comprises TaCl_5 ,
the first monolayer comprises TaCl_x , the second precursor gas comprises NH_3 , the second
monolayer comprises TaN , and the mass is formed to consist of TaN .

25

15. The method of claim 1 wherein the component of the first monolayer comprises a metal in elemental form.

16. The method of claim 1 wherein the second monolayer comprises a
30 conductive metal compound, and the mass of material is conductive.

17. The method of claim 1 wherein the second monolayer comprises a dielectric, and the mass of material is insulative.

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18. An atomic layer deposition method comprising:
positioning a semiconductor substrate within an atomic layer deposition chamber;
flowing a first precursor gas to the substrate within the chamber effective to
form a first monolayer on the substrate;

5 flowing a second precursor gas different in composition from the first precursor
gas to the first monolayer within the chamber under surface microwave plasma
conditions within the chamber effective to react with the first monolayer and form a
second monolayer on the substrate which is different in composition from the first
monolayer, the second monolayer comprising components of the first monolayer and the
10 second precursor; and

after the second precursor gas flowing, flowing a third precursor gas different
in composition from the first and second precursor gases to the second monolayer within
the chamber effective to react with the second monolayer and form a third monolayer
on the substrate which is different in composition from the first and second monolayers.

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19. The method of claim 18 successively repeating said first, second and third
precursor flowings effective to form a mass of material on the substrate comprising the
third monolayer composition.

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20. The method of claim 18 successively repeating said first, second and third
precursor flowings effective to form a mass of material on the substrate consisting
essentially of the third monolayer composition.

25

21. The method of claim 18 successively repeating said first, second and third
precursor flowings effective to form a mass of material on the substrate consisting of
the third monolayer composition.

30

22. The method of claim 18 wherein the first precursor gas comprises TiCl_4
and the first monolayer comprises TiCl_x .

23. The method of claim 18 wherein the first precursor gas comprises TiCl_4 ,
the first monolayer comprises TiCl_x , and the second precursor gas comprises H_2 .

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24. The method of claim 18 wherein the first precursor gas comprises TiCl_4 ,
the first monolayer comprises TiCl_x , the second precursor gas comprises H_2 , the third
precursor gas comprises NH_3 , and the third monolayer comprises TiN .

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25. The method of claim 18 wherein at least one of the first and third precursor gas flowings are void of plasma within the chamber.

26. The method of claim 18 wherein at least one of the first and third
5 precursor gas flowings are void of surface microwave plasma within the chamber.

27. The method of claim 18 wherein both the first and third precursor gas flowings are void of plasma within the chamber.

10 28. The method of claim 18 wherein at least one of the first and third precursor gas flowings are void of surface microwave plasma within the chamber.

29. The method of claim 18 wherein at least one of the first and third precursor gas comprises plasma within the chamber.

15

30. The method of claim 18 wherein at least one of the first and third precursor gas flowings comprise surface microwave plasma within the chamber.

31. The method of claim 18 wherein both the first and third precursor gas
20 flowings comprise plasma within the chamber.

32. The method of claim 18 wherein both of the first and third precursor gas flowings comprise surface microwave plasma within the chamber.

25 33. The method of claim 18 wherein the first monolayer is of a composition which is substantially unreactive with the second precursor under otherwise identical processing conditions but for presence of surface microwave plasma within the chamber.

34. The method of claim 18 wherein the first precursor gas comprises
30 trimethylaluminum and the first monolayer comprises AlCH_x .

35. The method of claim 18 wherein the first precursor gas comprises trimethylaluminum, the first monolayer comprises AlCH_x , and the second precursor gas comprises H_2 .

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36. The method of claim 18 wherein the first precursor gas comprises trimethylaluminum, the first monolayer comprises AlCH_x , the second precursor gas comprises H_2 , the third precursor gas comprise NH_3 , and the third monolayer comprises Al_2O_3 .

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37. The method of claim 18 wherein the first precursor gas comprises TaCl_5 and the first monolayer comprises TaCl_x .

38. The method of claim 18 wherein the first precursor gas comprises TaCl_5 ,
10 the first monolayer comprises TaCl_x , and the second precursor gas comprises H_2 .

39. The method of claim 18 wherein the first precursor gas comprises TaCl_5 ,
the first monolayer comprises TaCl_x , the second precursor gas comprises H_2 , the third
precursor gas comprises NH_3 , and the third monolayer comprises TaN .

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40. An atomic layer deposition method comprising:
positioning a semiconductor substrate within an atomic layer deposition chamber;
flowing a first precursor gas to the substrate within the chamber effective to
form a first monolayer on the substrate;

20 flowing a second precursor gas different in composition from the first precursor
gas to the first monolayer within the chamber under surface microwave plasma
conditions within the chamber effective to react with the first monolayer and form a
second monolayer on the substrate which is different in composition from the first
monolayer, the second monolayer comprising components of the first monolayer and the
25 second precursor; and

after the second precursor gas flowing, flowing the first precursor gas to the
substrate within the chamber effective to react with the second monolayer and both a)
remove a component of the second monolayer to form a third composition monolayer
on the substrate which is different in composition from the first and second monolayers;
30 and b) form a fourth monolayer of the first monolayer composition on the third
composition monolayer.

41. The method of claim 40 wherein the third composition monolayer
comprises a metal in elemental form.

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42. The method of claim 40 wherein the removed component comprises hydrogen.

43. The method of claim 40 wherein the removed component comprises
5 elemental hydrogen.

44. The method of claim 40 wherein the first precursor gas flowing is void of plasma within the chamber.

10 45. The method of claim 40 wherein the first precursor gas flowing is void of surface microwave plasma within the chamber.

46. The method of claim 40 wherein the first precursor gas flowing comprises plasma within the chamber.

15

47. The method of claim 40 wherein the first precursor gas flowing comprises surface microwave plasma within the chamber.

48. The method of claim 40 wherein the first monolayer is of a composition
20 which is substantially unreactive with the second precursor under otherwise identical processing conditions but for presence of surface microwave plasma within the chamber.

49. The method of claim 40 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , the second precursor comprises H_2 , and the third
25 composition monolayer comprises elemental titanium.

50. The method of claim 40 wherein the first precursor gas comprises TaCl_5 , the first monolayer comprises TaCl_x , the second precursor comprises H_2 , and the third composition monolayer comprises elemental tantalum.

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51. An atomic layer deposition method, comprising;
positioning a semiconductor substrate within an atomic layer deposition chamber;
flowing a first precursor gas to the substrate within the chamber effective to
form a first monolayer on the substrate;
- 5 after forming the first monolayer, flowing an inert purge gas to the chamber;
after flowing the inert purge gas, flowing a second precursor gas to the substrate
under plasma conditions within the chamber effective to form a second monolayer on
the substrate which is different in composition from the first monolayer, the second
precursor gas being different in composition from the first precursor gas, said plasma
10 conditions comprising application of energy to the chamber at a power level capable of
sustaining plasma conditions within the chamber with the second precursor gas; and
commencing application of said energy to the chamber at an increasing power
level up to said plasma capable power level prior to flowing the second precursor gas
to the chamber.
- 15
52. The method of claim 51 wherein the inert purge gas and second precursor
gas flowings do not overlap.
53. The method of claim 51 wherein the inert purge gas and second precursor
20 gas flowings overlap.
54. The method of claim 51 wherein the inert purge gas and second precursor
gas flowings overlap, and comprising ceasing the inert purge gas flowing after a ceasing
of the second precursor gas flowing.
- 25
55. The method of claim 51 comprising after forming the second monolayer,
commencing another inert purge gas flowing prior to commencing a reducing of the
plasma capable power.
- 30
56. The method of claim 55 wherein the second precursor and another inert
purge gas flowings do not overlap.
57. The method of claim 51 comprising ceasing flow of the second precursor
gas to the chamber prior to commencing a reducing of the plasma capable power.
- 35

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58. The method of claim 51 comprising:
after forming the second monolayer, commencing another inert purge gas flowing
prior to commencing a reducing of the plasma capable power; and
ceasing flow of the second precursor gas to the chamber prior to commencing
5 said reducing of the plasma capable power.

59. The method of claim 51 wherein the plasma conditions comprise surface
microwave plasma.

10 60. The method of claim 51 wherein said increasing is continuous.

61. The method of claim 51 wherein the first precursor gas comprises TiCl_4 ,
the first monolayer comprises TiCl_x , and the second precursor gas comprises H_2 .

15 62. The method of claim 51 wherein the first monolayer is formed in the
absence of plasma within the chamber.

63. The method of claim 51 wherein the second monolayer reacts with the
first monolayer, the second monolayer comprising components of the first monolayer and
20 the second precursor.

64. An atomic layer deposition method, comprising;
positioning a semiconductor substrate within an atomic layer deposition chamber;
flowing a first precursor gas to the substrate within the chamber effective to
25 form a first monolayer on the substrate;
after forming the first monolayer, flowing an inert purge gas to the chamber;
after flowing the inert purge gas, flowing a second precursor gas to the substrate
under plasma conditions within the chamber effective to form a second monolayer on
the substrate which is different in composition from the first monolayer, the second
30 precursor gas being different in composition from the first precursor gas, the second
precursor gas flowing under plasma conditions within the chamber commencing before
a ceasing of the inert purge gas flowing; and
ceasing the inert purge gas flowing after commencing and while said flowing of
the second precursor gas under plasma conditions within the chamber.

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65. The method of claim 64 comprising after forming the second monolayer, commencing another inert purge gas flowing prior to a ceasing of the second precursor gas flowing to the chamber.

5 66. The method of claim 64 wherein the plasma conditions comprise application of energy to the chamber at a power level capable of sustaining plasma conditions within the chamber with the second precursor gas; and commencing application of said energy to the chamber at an increasing power level up to said plasma capable power level commensurate with commencing flow of the second precursor gas
10 to the chamber.

67. The method of claim 64 wherein the plasma conditions comprise application of energy to the chamber at a power level capable of sustaining plasma conditions within the chamber with the second precursor gas; and commencing
15 application of said energy to the chamber at an increasing power level up to said plasma capable power level prior to commencing flow of the second precursor gas to the chamber.

68. The method of claim 64 wherein the plasma conditions comprise application of energy to the chamber at a power level capable of sustaining plasma conditions within the chamber with the second precursor gas; and commencing
20 application of said energy to the chamber at an increasing power level up to said plasma capable power level after commencing flow of the second precursor gas to the chamber.

25 69. The method of claim 64 wherein the plasma conditions comprise surface microwave plasma.

70. The method of claim 64 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , and the second precursor gas comprises H_2 .
30

71. The method of claim 64 wherein the second monolayer reacts with the first monolayer, the second monolayer comprising components of the first monolayer and the second precursor.

72. An atomic layer deposition method, comprising;
positioning a semiconductor substrate within an atomic layer deposition chamber;
flowing a first precursor gas to the substrate within the chamber effective to
form a first monolayer on the substrate;

5 after forming the first monolayer, flowing a second precursor gas to the substrate
under plasma conditions within the chamber effective to form a second monolayer on
the substrate which is different in composition from the first monolayer, the second
precursor gas being different in composition from the first precursor gas, plasma
generation of the second precursor gas within the chamber occurring from a second
10 applied power of energy to the chamber, and further comprising applying a steady state
first applied power of said energy to the chamber prior to applying said second applied
power of said energy, the steady state first applied power being less than the second
applied power and increasing the first applied power to said second applied power.

15 73. The method of claim 72 wherein said increasing is continuous.

74. The method of claim 72 wherein the steady state first power is
insufficient to generate plasma from flowing the second precursor gas.

20 75. The method of claim 72 wherein the steady state first power is
insufficient to generate plasma from flowing the first precursor gas.

76. The method of claim 72 comprising applying the steady state first power
during the first precursor flowing.

25 77. The method of claim 76 wherein the steady state first power is
insufficient to generate plasma from the flowing first precursor gas.

78. The method of claim 72 comprising flowing an inert purge gas to the
30 chamber intermediate the first and second precursor gas flowings.

79. The method of claim 78 comprising applying the steady state first power
during the inert purge gas flowing.

80. The method of claim 78 comprising flowing an inert purge gas to the chamber after the second precursor gas flowing, applying the steady state first power during the inert purge gas flowing intermediate the first and second precursor gas flowings and applying the steady state first power during the inert purge gas flowing
5 after the second precursor flowing.

81. The method of claim 72 wherein the plasma conditions comprise surface microwave plasma.

10 82. The method of claim 72 comprising commencing the increasing prior to commencing the second precursor gas flowing.

83. The method of claim 72 comprising commencing the increasing after commencing the second precursor gas flowing.

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84. The method of claim 72 comprising commencing the increasing commensurate with commencing the second precursor gas flowing.

85. The method of claim 72 comprising reducing power to the steady state
20 first power after a ceasing flow of the second precursor gas.

86. The method of claim 72 comprising reducing power to the steady state first power prior to a ceasing flow of the second precursor gas.

25 87. The method of claim 72 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , and the second precursor gas comprises H_2 .

88. An atomic layer deposition method, comprising;
positioning a semiconductor substrate within an atomic layer deposition chamber;
applying a base power level of energy to the chamber with the substrate
positioned therein;

5 while applying the base power level of energy, flowing a first precursor gas to
the substrate within the chamber effective to form a first monolayer on the substrate
under non-plasma conditions within the chamber;

after forming the first monolayer, raising the base power level of said energy to
a power level capable of generating plasma within the chamber;

10 flowing a second precursor gas to the substrate within the chamber while said
plasma capable power level of said energy is applied to the chamber effective to form
a plasma with said second precursor gas against the first monolayer to form a second
monolayer on the substrate which is different in composition from the first monolayer;
and

15 after forming the second monolayer, reducing the plasma capable power level of
said energy to the base power level and thereafter depositing another monolayer onto
the second monolayer.

89. The method of claim 88 wherein said raising is continuous.

20

90. The method of claim 88 comprising flowing an inert purge gas to the
chamber intermediate the first and second precursor gas flowings.

91. The method of claim 90 comprising applying the base power level of
25 energy during the inert purge gas flowing.

92. The method of claim 90 comprising flowing an inert purge gas to the
chamber after the second precursor gas flowing, applying the base power level of energy
during the inert purge gas flowing intermediate the first and second precursor gas
30 flowings and applying the base power level of energy during the inert purge gas flowing
after the second precursor flowing.

93. The method of claim 88 wherein the plasma comprises surface microwave
plasma.

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94. The method of claim 88 comprising commencing the raising prior to commencing the second precursor gas flowing.

95. The method of claim 88 comprising commencing the raising after
5 commencing the second precursor gas flowing.

96. The method of claim 88 comprising commencing the raising commensurate with commencing the second precursor gas flowing.

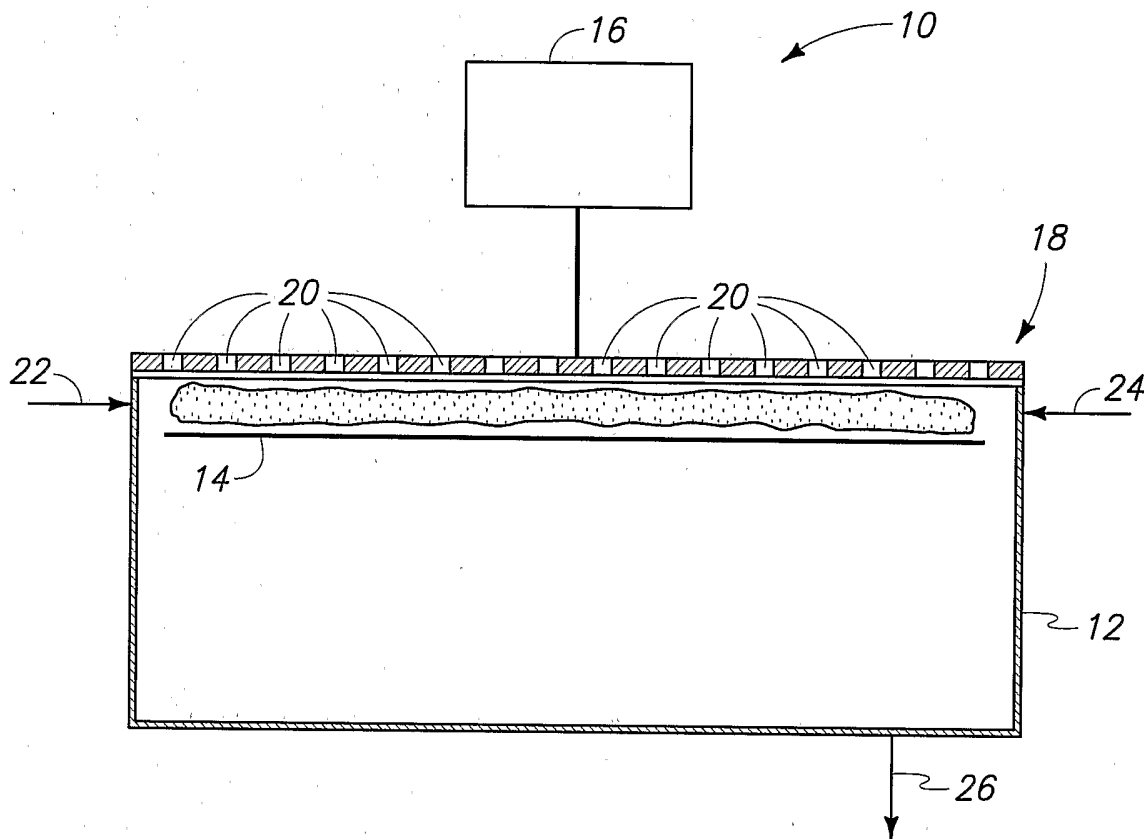
10 97. The method of claim 88 comprising commencing said reducing after a ceasing flow of the second precursor gas.

98. The method of claim 88 comprising commencing said reducing prior to a ceasing flow of the second precursor gas.

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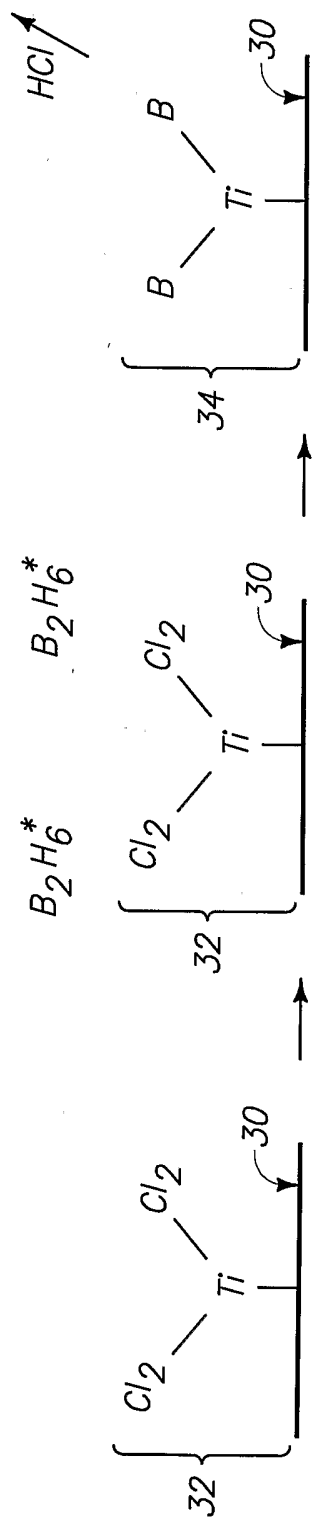
99. The method of claim 88 wherein the first precursor gas comprises TiCl_4 , the first monolayer comprises TiCl_x , and the second precursor gas comprises H_2 .

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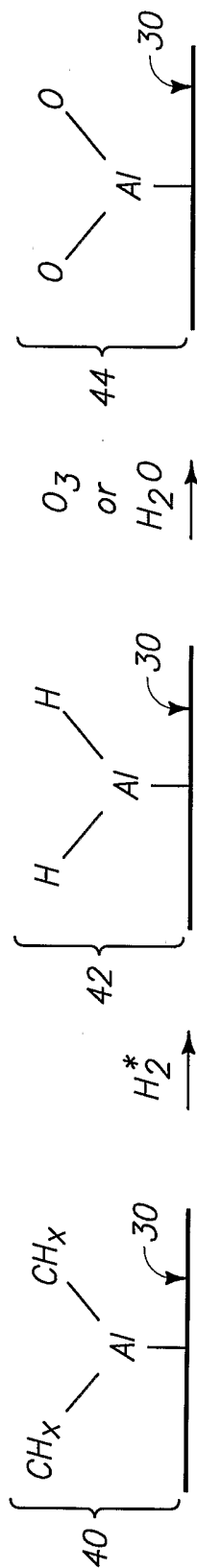


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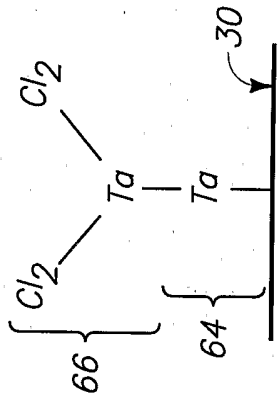


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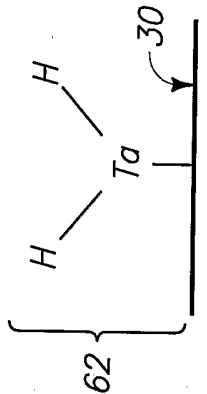


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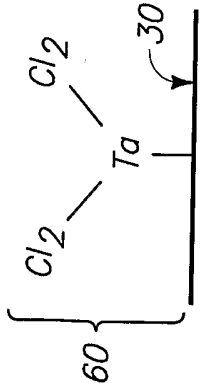
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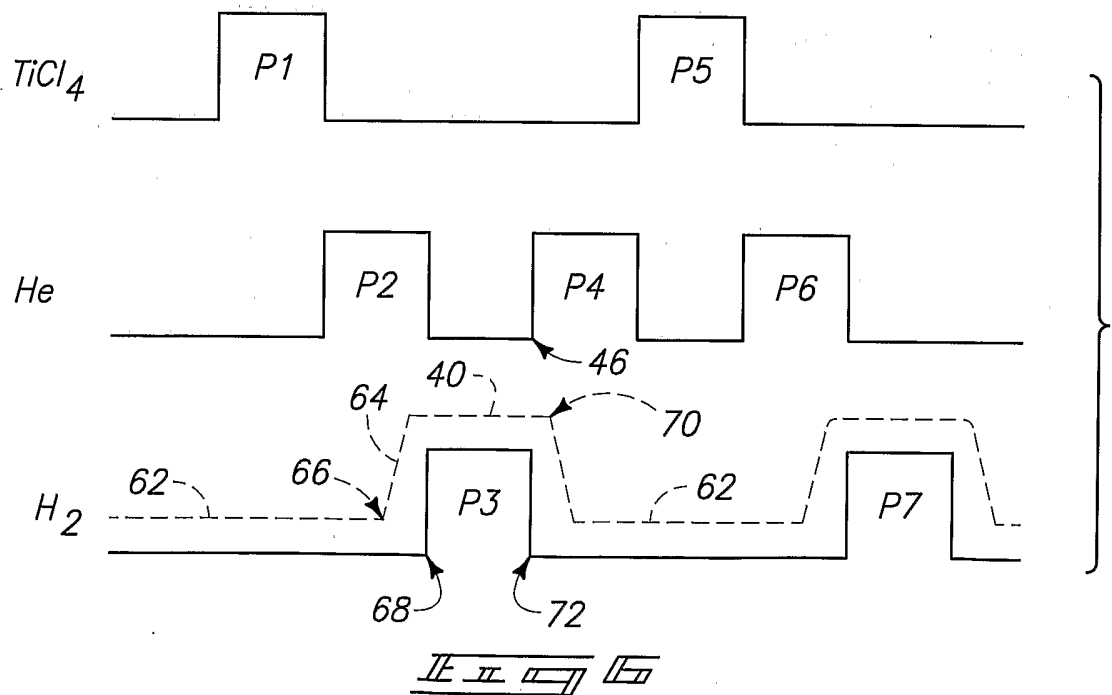
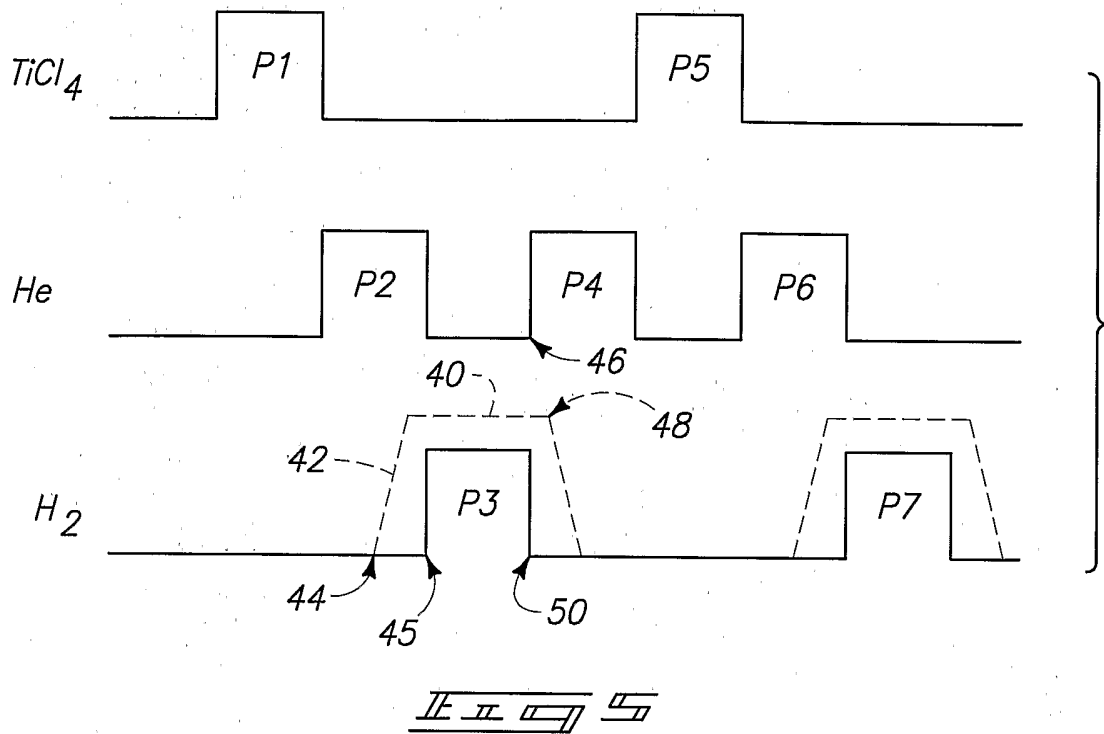
TaCl₅ →



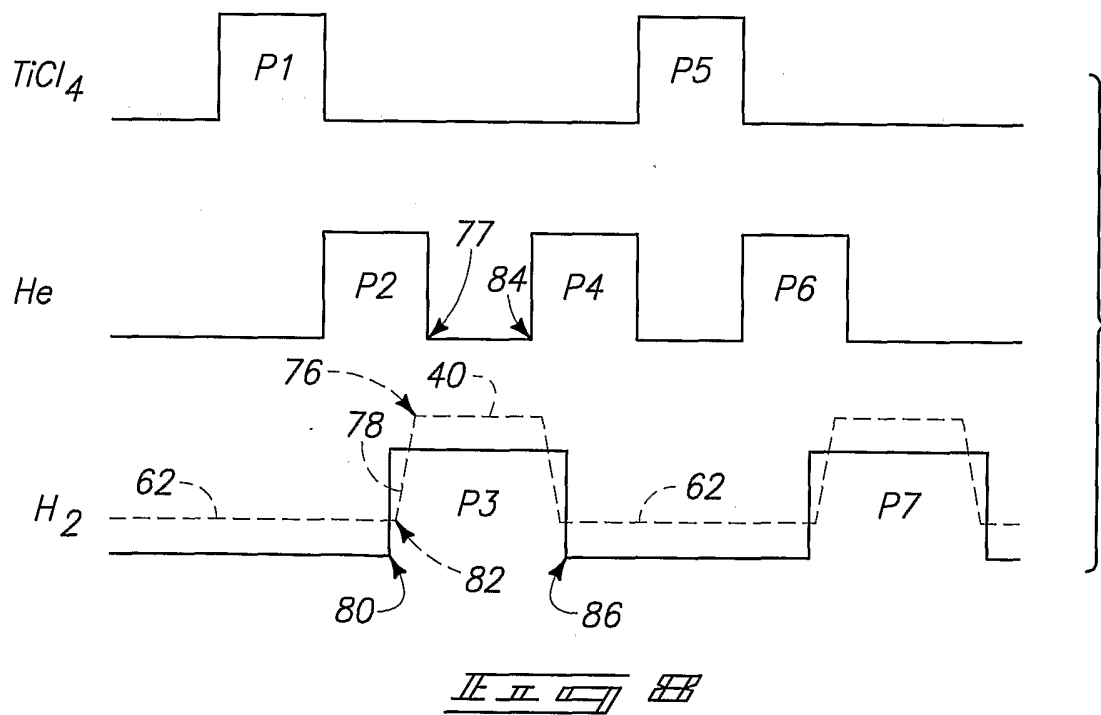
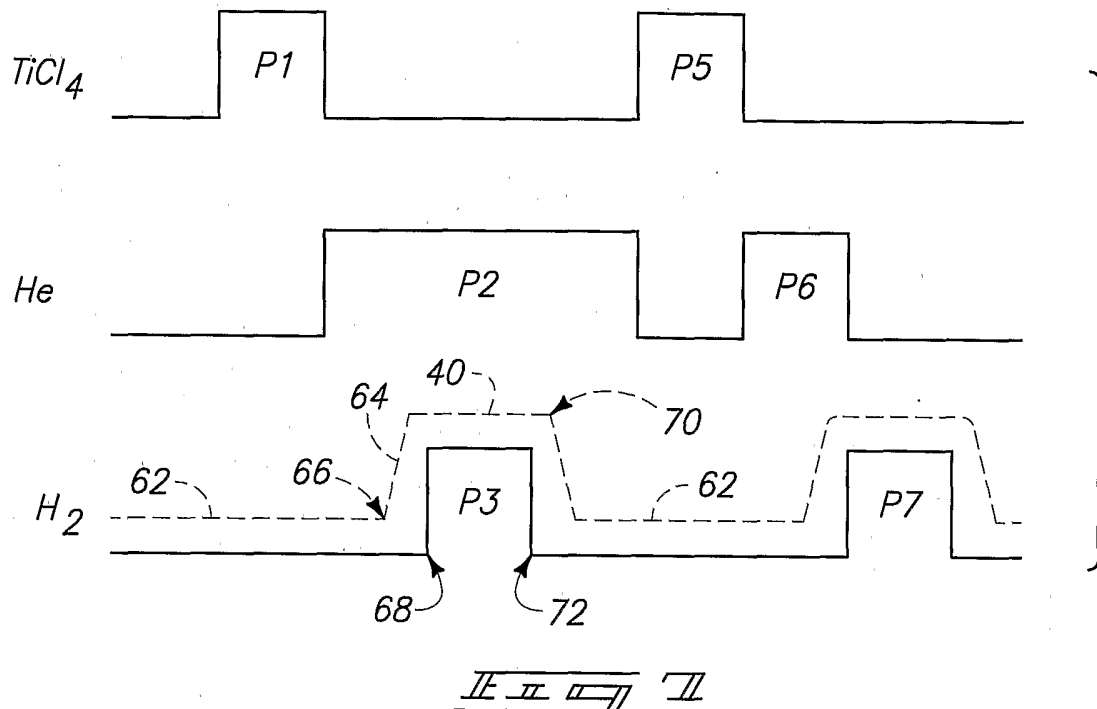
H₂^{*} →



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