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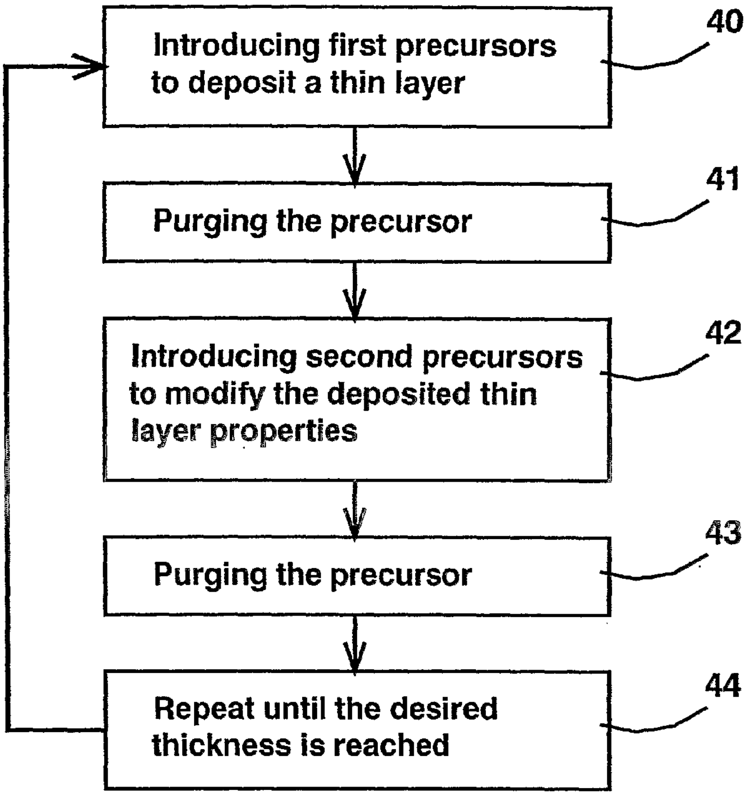

(57) Abstract: A hybrid deposition process of CVD and ALD, called NanoLayer Deposition ("NLD") is provided. The nanolayer deposition process is a cyclic sequential deposition process, comprising the first step of introducing a first plurality of precursors to deposit a thin film with the deposition process not self-limiting, then a second step of purging the first set of precursors and a third step of introducing a second plurality of precursors to modify the deposited thin film. The deposition step in the NLD process using the first set of precursors is not self-limiting and is a function of substrate temperature and process time. The second set of precursors modifies the already-deposited film characteristics. The second set of precursors can treat the deposited film such as a modification of film composition, a doping, or a removal of impurities from the deposited film. The second set of precursors can also deposit another layer on the deposited film. The additional layer can react with the existing layer to form a compound layer, or can have minimum reaction to form a nanolaminate film.

WO 2004/070074 A2

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NANOLAYER DEPOSITION PROCESS

Claim to Priority

[0001] This application claims priority to U.S. Patent Application No. 10/360,135, filed February 4, 2003, which is incorporated herein by reference.

Background of the Invention

[0002] The present invention relates to the deposition of a thin film and specifically to semiconductor thin film processing.

[0003] Deposition is one of the basic fabrication processes of modern semiconductor device structures. Deposition techniques includes Physical Vapor Deposition ("PVD," or sputtering), and Chemical Vapor Deposition ("CVD") and numerous variations of CVD such as pulsed CVD, sequential CVD, or Atomic Layer Deposition ("ALD").

[0004] PVD process uses a high vacuum apparatus and generated plasma that sputters atoms or clusters of atoms toward the surface of the wafer substrates. PVD is a line-of-sight deposition process that is more difficult to achieve conforming film deposition over complex topography, such as deposition of a thin and uniform liner or barrier layer over a small trench or via of 0.13 μm or less, especially with a high aspect ratio greater than 4:1.

[0005] CVD method is different from PVD method. In CVD, a gas or vapor mixture is flowed over the wafer surface at an elevated temperature. Reactions then take place at the hot surface where deposition takes place. The basic characteristic of a CVD process is the reaction at the substrate of all the precursor vapors together. The reaction often requires the presence of an energy source such as thermal energy (in the form of resistive heated substrate, or radiative heating), or plasma energy (in the form of plasma excitation). Temperature of the wafer surface is an important factor in CVD deposition, because the deposition depends on the reaction of the precursors and affects the uniformity of deposition over the large wafer surface. CVD typically requires high temperature for deposition which may not be compatible with other processes in the semiconductor process. CVD at lower temperature tends to produce low quality films in term of uniformity and impurities. The reactions can be further promoted by plasma energy in plasma enhanced CVD process, or by photon energy in rapid thermal CVD process. CVD technology has been used in semiconductor processing for a long time, and its characteristics are well known with a variety of precursors available. However, CVD does not meet modern technology requirements for new materials and more stringent film qualities and properties.

[0006] Variations of CVD include pulse CVD or sequential CVD. In pulse or sequential CVD, the chemical vapors or the supplied energies, such as plasma energy, thermal energy, and laser energy, are pulsed instead of continuous, as in CVD process. The major advantages of pulse CVD is the high effects of the transient state resulted from the on-off status of the precursors or the energies, and the reduced amount of precursors or energies owing to the pulsed mode. Reduced energy, which can be accomplished in pulse mode, is desirable because it causes less substrate damage such as the case of plasma processing for thin gate oxide. The reduced precursor amount for pulse mode is desirable for specific applications, such as epitaxial deposition, where the precursors need to react with the substrate to extend the single crystal nature of the substrate in a specific arrangement. There are no purging steps in pulse CVD, since cross-contaminations or gas phase reactions are not a concern, and the purpose of the pulsing of the precursors or energies is to obtain the desired film characteristics.

[0007] Pulse CVD can be used to create gradient deposition, such as U.S. patent No. 5,102,694 of Taylor et al. ("Taylor"). Taylor discloses a pulsed deposition process in which the precursors are periodically reduced to create a gradient of composition in the deposited films. Taylor's pulsed CVD relies only on the changing of the first set of precursors to vary the film compositions.

[0008] Pulsed CVD can be used to modulate precursor flow, as disclosed in U.S. patent No. 5,242,530 of Batey et al. ("Batey"), entitled "Pulsed gas plasma-enhanced chemical vapor deposition of silicon." Batey discloses a pulsed deposition process in which the precursor silane is modulated during a steady flow of plasma hydrogen. The pulsing of silane creates a sequence of deposition and without the silane pulses, the steady plasma hydrogen cleans and prepares the deposited surface.

[0009] Pulsed CVD can be used to pulse the plasma energy needed for the deposition process, as disclosed in U.S. patent No. 5,344,792 of Sandhu et al. ("Sandhu"), entitled "Pulsed plasma enhanced CVD of metal silicide conductive films such as $TiSi_2$." Sandhu discloses a pulsed deposition process in which the precursors are introduced into a process chamber, then the plasma energy is introduced in pulsed mode to optimize the deposition conditions. U.S. patent No. 5,985,375 of Donohoe et al. ("Donohoe"), entitled "Method for pulsed plasma enhanced vapor deposition," discloses a similar pulsed CVD process with the plasma energy in pulsed mode but with a power-modulated energy waveform. The pulsing of the plasma energy allows the deposition of a metal film with desired characteristics. U.S. patent No. 6,200,651 of Roche et al. (“Roche”), entitled "Method of chemical vapor deposition in a vacuum plasma processor responsive to a pulsed microwave source," discloses a pulsed CVD process with an electron cyclotron resonance plasma having a repetitive pulsed microwave field to optimize the deposited films. U.S. patent No. 6,451,390 of Goto et al. (“Goto”), entitled "Deposition of TEOS oxide using pulsed RF plasma," discloses a tetraethoxysilane (“TEOS”) oxide deposition process using a pulsed RF plasma to control the deposition rate of silicon dioxide. The pulsing feature offers the optimization of the deposit films through the transient state instead of the steady state. Pulsing of plasma during nitridation process of gate oxide shows less damage than continuous plasma nitridation process because of higher interaction owing to plasma transient state, and less damage as a result of shorter plasma time.

[0010] Pulsed CVD can be used to pulse the precursors needed for the deposition process such as U.S. patent No. 6,306,211 of Takahashi et al. (“Takahashi”), entitled "Method for growing semiconductor film and method for fabricating semiconductor devices.” Takahashi discloses a pulsed CVD process to deposit epitaxial film of $Si_xGe_yC_z$. Epitaxial deposition requires a single crystal substrate, and the deposited film extends the single crystal nature of the substrate, different from CVD poly-crystal or amorphous film deposition. To extend the single crystal nature of the substrate, the deposited precursors need to bond with the substrate at specific lattice sites. A reduced precursor flow thus is highly desirable in epitaxial deposition because it allows the precursors sufficient time to arrange into a correct lattice. The process includes a continuous flow of hydrogen to dilute the precursors to be introduced. Then sequential pulses of silicon-based precursor, germanium-based precursor and carbon-based precursor are introduced to deposit an epitaxial film of $Si_xGe_yC_z$.

To deposit epitaxial film, small amounts of precursors are needed. This can be accomplished by short pulses (on the order of micro-seconds). The precursors can be further diluted in a high flow of hydrogen. Takahashi discloses that the pulses of the precursors are not overlapped, but is silent on the separation of these pulses. The objective of Takahashi's pulsed CVD is to deposit compound films. Therefore the separation of these precursors is not relevant.

[0011] Pulsed CVD, as described by Takahashi, to deposit epitaxial film of $Si_xGe_yC_z$, does not allow deposition of high coverage or conformal film on a non-flat substrate, such as in a via or trench for interconnects in semiconductor devices. The objective of Takahashi's pulsed CVD is to deposit epitaxial films with sufficiently planar surface as observed by Takahashi, without mention of possible deposition on trenches or vias.

[0012] ALD is another variation of CVD using chemical vapor for deposition. In ALD, various vapors are injected into the chamber in alternating and separated sequences. For example, a first precursor vapor is delivered into the chamber to be adsorbed onto the substrate. Then the first vapor is turned off and evacuated from the chamber. Another precursor vapor is then delivered into the chamber to react with the adsorbed molecules on the substrate to form a desired film. Then this second vapor is turned off and evacuated from the chamber. This sequence is repeated for many cycles until the deposited film reaches the desired thickness. There are numerous variations of ALD processes, but the ALD processes all share two common characteristics: (1) sequential precursor vapor flow and (2) self-limiting thickness per cycle. The sequential precursor flow and evacuation characteristic eliminates the gas phase reaction commonly associated with the CVD process. The characteristic of self-limiting thickness per cycle offers excellent surface coverage, because the total film thickness does not depend on precursor flow, nor on process time. The total film thickness depends only on the number of cycles. The ALD process is not sensitive to the substrate temperature.

[0013] The maximum thickness per cycle of ALD process is one monolayer because of the self limiting feature that the substrate surface is saturated with the first precursor. The first precursor can adsorb onto the substrate, or the first precursor can have some reaction at the substrate, but the first precursor also saturates the substrate surface and the surface is terminated with a first precursor ligand.

[0014] The throughput of the ALD process depends on how fast a cycle is. Therefore a small chamber volume is critical. Furthermore, fast switching of the precursor valves is desirable to allow a high throughput. A typical ALD cycle is a few seconds long. Therefore the precursor pulses are on the order of seconds. Precursor depletion effect can be severe for this short process time.

[0015] United States Patent No. 5,916,365 to Sherman ("Sherman"), entitled "Sequential chemical vapor deposition," provides for sequential chemical vapor deposition (ALD) by a sequence of chamber evacuation, adsorption of the first precursor onto the substrate, followed by another chamber evacuation, and then by a second radical precursor to react with the adsorbed precursor on the substrate surface, and a third chamber evacuation. The Sherman process produces sub-monolayers per cycle due to adsorption. The process cycle can be repeated to grow the desired thickness of film. Sherman discloses an ALD process in which the first precursor process flow is self-limiting, meaning that no matter how long the process is, the adsorption thickness cannot changed. United States Patent No. 6,015,590 to Suntola et al. ("Suntola"), entitled "Method for growing thin films," discloses an ALD process which completely separates the precursors. The disclosed Suntola process is an improved ALD process (called atomic layer epitaxy ("ALE") by Suntola) meaning the deposition is achieved through the saturation of precursors on the substrate surface and the subsequent reaction with the reactants. The advantage of the Suntola process is the complete separation of precursors, with a better than 99% purging between pulses of precursors to prevent cross reactions.

[0016] United States Patent No. 6,200,893, and its divisions (U.S. patent No. 6,451,695, U.S. patent No. 6,475,910, U.S. patent publication No. 2001/0002280, U.S. patent publication 2002/0192954, U.S. patent publication No. 2002/0197864) to Sneh, entitled “Radical-assisted sequential CVD,” discuss a method for ALD deposition. The Sneh sequence process is a variation of the ALD process. Sneh discloses a deposition step for the first precursor introduction, but the deposition of Sneh is self-limiting because of the surface saturation with ligands. In fact, in U.S. patent No. 6,475,910, Sneh discloses a method to extend the thickness of the first precursor introduction step. The disclosure discloses another ALD process to sequential precursor flows to increase the thickness of the first precursor introduction step. In some respects, this is similar to a nested loop, where the thickness of the first precursor flow step of an ALD process can be increased by another ALD process.

Summary of the Invention

[0017] The present invention provides a hybrid deposition process of CVD and ALD, called NanoLayer Deposition (“NLD”). A co-pending application "Nanolayer thick film processing system and method" of the same inventors, serial number 09/954,244, filing date September 10, 2001, Publication No. 2003/0049375 A1, published March 13, 2003.

[0018] In one aspect of the invention, the present invention method to deposit a thin film on a substrate that comprises the steps of:

a. introducing into a chamber a first plurality of precursors to deposit a first layer on a substrate in a non-self-limiting deposition process;

b. purging the first precursors; and

c. introducing a second different plurality of precursors that modify the deposited first layer in a modification process, wherein at least one precursor of the second plurality of precursors differs from those of the first plurality of precursors.

[0019] The deposition step in the present invention is not self-limiting and is a function of substrate temperature and process time. This first step is similar to a CVD process using a first set of precursors. Then the first set of precursors is turned off and purged from the process chamber and a second set of precursors is introduced. The purpose of the purging step is to avoid the possible interaction between the two sets of precursors. Therefore the purging can be accomplished by a pumping step to evacuate the existing precursors from the process chamber. The characteristic of the pumping step is the reduction in chamber pressure to evacuate all gases and vapors. The purging can also be accomplished by a replacement step by using a non-reacting gas, such as nitrogen or inert gas, to push all the precursors out of the process chamber. The replacement step maintains the chamber pressure, with the precursor turned off and the purge gas turned on. A combination of these two steps can be use in the purging step, such as a pumping step followed by a nitrogen or argon replacement step.

[0020] The second set of precursors modifies the already deposited film characteristics. The second set of precursors can treat the deposited film by, for example, a modification of film composition, a doping, or a removal of impurities from the deposited film. The second set of precursors can also deposit another layer on the deposited film. The additional layer can react with the existing layer to form a compound layer, or can have minimum reaction to form a nanolaminate film. In one preferred embodiment, the deposition step is preferably a disordered film deposition, in contrast to an ordered film deposition, as in an epitaxial film. Deposition conditions for disordered film deposition are much simpler to achieve with less initial surface preparation and fewer special considerations relating to the order of the deposited films. In ordered film deposition, like epitaxial film deposition, small amounts of precursors are typically used to allow the precursors sufficient time to arrange themselves on the surface to form crystalline film. For that purpose, pulsed CVD is highly suited for epitaxial film deposition. The epitaxial deposition also requires a buffer layer to ensure a continuous lattice growth, especially with a dissimilar lattice structure of the substrate and the deposited film.

[0021] The present NLD method to deposit a film differs markedly from CVD method with a sequential process and with the introduction of the second set of precursors. The present NLD method differs from pulse or sequential CVD with a purging step and with the introduction of the second set of precursors. The introduction of the second set of precursors after purging the first precursors in a cyclic sequential process allows the modification of the deposited film in a manner not possible in CVD and pulse and sequential CVD methods.

[0022] The pulsed CVD processes, employing the pulsing of precursors to modify the composition such as gradient of the deposited films, differ from the present invention NLD process because they lack the second set of precursors to modify the properties of the deposited films.

[0023] The pulsed CVD processes employing the pulsing of deposition precursors in the presence of plasma precursors to modify the deposited film characteristics, such as a smoother surface, differ from the present invention NLD process because they lack the purging step between the pulses, and because the plasma precursors are present throughout the deposition time. This pulsed CVD process allows the mixture of the continuous plasma precursors and the deposition precursors. In contrast, the NLD process offers a purging step between the two sets of precursors to avoid cross contamination, to avoid possible gas phase reaction, and to prepare the process chamber for different processes. For example, the purging step clears out the precursor, such as a metal-organic chemical vapor deposition ("MOCVD") precursor, before turning on the plasma because the plasma is difficult to strike in the presence of a vapor.

[0024] The pulsed CVD processes, employing the pulsing of plasma energy to modify the deposited film characteristics, such as smoother film, different deposition rate, less damage to the deposited films, differ from the present invention NLD process because they lack the second set of precursors to modify the properties of the deposited films. They also lack the purging step between the pulses. The pulsing feature offers the optimization of the deposit films through the transient state instead of the steady state, and therefore differ significantly with the present invention NLD method of using the second set of precursors to modify the deposited film characteristics.

[0025] The pulsed CVD processes employing the pulsing of deposition precursors to form epitaxial film differ from the present invention NLD process because they lack the purging step between the precursors pulses. The purging step allows the use of incompatible precursors due to the separation effect of the purging step. The differences between pulsed CVD and NLD also include the conceptual purpose of the two methods. The objective of pulsed CVD is to employ a suitable set of precursors and conditions to deposit the desired films, while the objective of NLD is to deposit a film, even an undesired film, and to provide a modification and treatment step to convert the undesired film into a desired film. Rather than finding a way to deposit a film with all the desired characteristics, as in CVD or pulsed CVD, NLD instead finds a way to treat or modify an existing film to achieve a film with the desired characteristics. Further, recognizing that treating and modifying an existing film is difficult with greater thickness, NLD offers a cyclic process of depositing and treating or modifying, so that the treatment process is performed on very thin film and to achieve a thicker film.

[0026] The present NLD method to deposit a film also differs markedly from the ALD method because NLD uses non-self-limiting deposition. The deposition step in the present invention NLD method is a function of substrate temperature and process time. The deposition/adsorption step in the ALD method, in contrast, is a self-limiting step based on the saturation of precursor ligands on the substrate surface. Once the surface is saturated, the deposition/adsorption in the ALD method stops, and any excess precursor vapors have no further effect on the saturated surface. In other words, the deposition/adsorption step of the ALD method is independent of time after reaching saturation. The ALD method also has less dependence on substrate temperature than CVD or NLD methods. Therefore the present invention NLD method is different in many ways from the ALD method.

[0027] In another aspect of the present invention, the method of deposition further comprises a last purging step, after step (c). Similarly to the previous purging step, the last purging step is to remove the second set of precursors from the process chamber, either by evacuation, replacement, or any combination. In many applications, the treatment step can only treat a thin film, or the treatment step is much more effective if treating only a thin film. Therefore the present invention further comprises a further step of repeating the previous steps until a desired thickness is reached. The last purging step can be optional because its purpose is to prevent possible reaction between two sets of precursors. In cases where there are minimal reactions between two sets of precursors, the last purging step can be eliminated to have a shorter process time and higher throughput.

[0028] The present invention also provides for the extension to a plurality of other sets of precursors. Another third set of precursors would enhance the modification of the deposited film at the expense of process complexity and lower throughput. Another two sets of precursors would create a multilayer thin film or a nanolaminate film.

[0029] The present invention NLD process can be performed in any process chamber such as a standard CVD process chamber or an ALD small volume, fast switching valve process chamber. The chamber wall can be cold wall, warm wall, or hot wall, depending on the desired outputs. The delivery system can be showerhead delivery to provide uniform flow, or a sidewall inlet to provide laminar flow, or a shower ring to offer circular delivery. The precursor delivery can be liquid injection where the liquid precursors are delivered to a heated vaporizer to convert the precursors into vapor form before delivering into the process chamber. The precursor delivery can be vapor draw where the vapor of a liquid precursor is drawn from the liquid precursor container. The precursor delivery can be by a bubbler where the vapor of the liquid precursor is enhanced with the bubbling feature of a non reactive carrier gas.

[0030] The steps in the present invention can be any CVD deposition step such as thermally activated CVD, plasma-enhanced CVD using parallel plate plasma, inductively coupled plasma ("ICP"), microwave plasma, remote plasma, or rapid thermal processing using lamp heating. Not only the deposition step, but also the treatment step can be a CVD deposition step to modify the deposited film properties.

[0031] The treatment step can be a plasma treatment, or a temperature treatment. The plasma treatment can be an energetic species, and can be further enhanced with a bias to give kinetic energy to the energetic species. A strong bias can create reaction such as an ion implantation, as in immersion ion implantation technology. In general, a highly energetic species in the treatment step can help in modifying the deposited film properties. A bombardment of species can be employed to improve the roughness of the deposited film. A chemical reaction can be employed to remove impurities or to change film compositions and to modify the physical properties, such as film density.

[0032] The present invention method can use any CVD precursors or MOCVD precursors. The deposition step is further enhanced with the second set of precursors to allow film properties that are difficult or impossible with CVD method. The precursors can be thermally activated, plasma activated, or rapid thermal process ("RTP") activated. The precursors can be hydrogen, nitrogen, oxygen, ozone, inert gas, water, or inorganic precursors such as NH_3, SiH_4, NF_3, or metal precursors such as $TiCl_4$, or organic precursors, or metal organic precursors such as tetrakisdimethyl titanium ("TDMAT"), tetrakisdiethyl titanium ("TDEAT"), tetrakis (methylethylamino) titanium ("TMEAT"), penta-dimethyl-amino-tantalum ("PDMAT"), and pentakis(diethylamido)tantalum ("PDEAT").

[0033] In general, the process temperature of the present invention is lower than the temperature of similar CVD process to obtain the lower deposition rate and better uniformity. A typical process temperature is between 100°C to 1000°C, depending on the thermal budget of the overall process. Metal interconnect of a semiconductor process requires the process temperature to be less than 500°C, and the new low dielectric constant (low k) interlevel dielectric process requires the process temperature to be less than 400°C, or even 350°C. For device fabrication, the temperature can be higher, up to 600°C, or even 800°C.

[0034] The process time of the present invention of each step is between the range of msec to many minutes. Shorter process time is desirable, but too short a process time can create many reliability issues, such as timing requirements and component requirements. A typical throughput of 10 to 60 wafers per hour is acceptable for semiconductor fabrication. Using about 4 to 20 cycles per film thickness, that translates to about 3 to 90 seconds per step.

[0035] One aspect of the present invention is the plasma energy. To treat the sidewall surface of a high aspect ratio trench, the plasma is a high density and high pressure plasma. High density plasma can be accomplished with ICP or microwave. High density plasma can also be accomplished with remote plasma.

[0036] High pressure plasma can be a little harder. High density and high pressure plasma require a high energy in the chamber volume to compensate for the high collision loss due to the presence of many charged and neutral particles. To increase the power delivered to the chamber volume, an ICP power source must be close to the chamber volume and contain many inductive segments. These two requirements are difficult to fulfill because as the number of inductive segments increases, the segments are farther away from the chamber volume due to the size of the inductive segments. The inductive segments are typically a coil for the plasma source and carry a large current, therefore need to be water cooled. Conventional inductive coil has cross section of a square or a circle with a hollow center for water cool flow. The increase in number of inductive coil turns will increase the power, but since the successive turns are farther away from the chamber, the power increase is somewhat reduced. At a certain distance, the power increase is no longer significant. Our plasma inductive coil is an innovative design and has a ribbon-like cross section with the width is many times larger than the thickness. A co-pending application " *Plasma semiconductor processing system and method*" of the same authors, serial number 09/898,439, filing date July 5, 2001, has been disclosed and has been published (Publication No. 2003/0008500 A1, dated January 9, 2003).

[0037] With the much reduced thickness of the helical ribbon inductive coil, on the order of 1 mm as compared to 5 or 10 mm for a conventional inductive coil, the inductive coils are much closer to the chamber volume and therefore can deliver high power to the process chamber, resulting in a high density, high pressure plasma for sidewall structure treatments. The heat removal issue of the helical ribbon differs from the conventional inductive coils. With this new source of plasma, our process chamber pressure can be as high as 1000 milliTorr, and with further improvement, can reach 5 Torr, as compared to the typical process pressure of 10 to 100 milliTorr. As a result, the sidewall treatment of our process can be very good and the result is close to 100% conformality at the sidewall and the top and bottom surface.

Brief Description of the Drawings

[0038] Fig. 1 is a flowchart of a prior art CVD process.

[0039] Fig. 2 is a flowchart of a prior art pulse CVD process.

[0040] Fig. 3 is a flowchart of a prior art ALD process.

[0041] Fig. 4 is a flowchart of the present invention NLD process.

Detailed Description of the Invention

[0042] Fig. 1 shows a flowchart of a prior art CVD process. In step 10, the precursors are introduced into the process chamber. The precursors are then reacted at the substrate surface to form a deposited film in step 11. The conditions for the precursors reaction can include plasma energy, thermal energy, photon energy, laser energy. The deposition characteristics of CVD process is the non-self-limiting nature, meaning film thickness increases with process time and substrate temperature.

[0043] Fig. 2 shows a flowchart of a prior art pulse CVD process. In step 20, the precursors are introduced into the process chamber in pulses. The precursors are then reacted at the substrate surface to form a deposited film in step 21. Similar to CVD process, pulse CVD process can incorporate plasma energy, thermal energy, photon energy, laser energy. The pulse CVD process conditions can include precursor pulsing, plasma pulsing, thermal energy pulsing, photon energy pulsing, and laser energy pulsing. The deposition characteristics of pulse CVD process is the repeated CVD deposition process.

[0044] Fig. 3 shows a flowchart of a prior art ALD process. In step 30, the precursors are introduced into the process chamber. Then the precursors are purged from the process chamber in step 31. Another set of precursors is introduced into the process chamber in step 32. Then this set of precursors is purged from the process chamber in step 33. This purging step 33 is optional. The sequence can be repeated in step 34 until a desired thickness is reached. The basic characteristics of ALD process is the saturation of precursors in step 31, meaning the deposition or adsorption of precursors in this step is self-limiting, and is sensitive to process time and substrate temperature. The two sets of precursors are reacted in step 32 after the introduction of the second set of precursors. The purging step 31 is required to separate the two sets of precursors to prevent gas phase reaction and to preserve the surface reaction of ALD process.

[0045] Fig. 4 shows a flowchart of the present invention NLD process. In step 40, the precursors are introduced into the process chamber. Then the precursors are purged from the process chamber in step 41. Another set of precursors is introduced into the process chamber in step 42. Then this set of precursors is purged from the process chamber in step 43. This purging step 43 is optional. The sequence can be repeated in step 44 until a desired thickness is reached. The basic characteristics of NLD process is the non self limiting nature of the deposition in step 41, meaning the deposition of precursors in this step is dependent on process time and substrate temperature. The two sets of precursors are not reacted with each other in step 42. Instead, the second set of precursors react with the products of the first set of precursors, resulting after step 40. The purging step 41 is normally needed to separate the two sets of precursors to prevent gas phase reaction, but may not be required in all cases because the NLD process does not depend on the two sets of precursors interacting.

[0046] The present NLD method to deposit a film differs significantly from CVD method with a sequential process and with the introduction of the second set of precursors. The present NLD method differs from pulse or sequential CVD with a purging step and with the introduction of the second set of precursors. The cyclic sequential deposition using two sets of precursors with a purging step separating these two sets of precursors allows the modification of the deposited film in a manner not possible in CVD and pulse and sequential CVD methods. The following examples discuss the advantages of NLD versus CVD. The term CVD refers to both pulse CVD and sequential CVD methods.

[0047] One example of such and advantage is the surface coverage property of a deposited film. A typical CVD process would run at high temperature and continuously until a film is deposited. The uniformity and surface coverage of the CVD process depends solely on the reaction mechanism of the chemical precursors and the initial substrate surface. In contrast, the NLD method of the present invention provides a second set of precursors to modify the substrate surface characteristics during the deposition time, effectively allowing a substrate surface similar to the initial surface at all times, to prevent surface property changes during the deposition process. The NLD method offers an extra controllability to modify the substrate surface during deposition time to improve the surface coverage property of the deposited film. An NLD silicon dioxide deposition using TEOS and oxygen as the first set of precursors and plasma argon or hydrogen or nitrogen as the second set of precursors offers more uniformity and surface coverage at a thin film than CVD process using TEOS/oxygen alone. Similarly, an NLD silicon nitride deposition process using silane/ammonia as a first precursors and plasma argon or hydrogen or nitrogen as the second set of precursors offers more uniformity and surface coverage at a thin film than CVD process using silane/ammonia alone.

[0048] Another example of the advantage of NLD over CVD is the process temperature of a deposited film. The CVD process temperature is determined by the reaction mechanism to provide an acceptable quality film. The lower process temperature in CVD process could change the deposited film properties, such as impurity incorporation due to incomplete reaction, different stoichiometry of the film components. In contrast, the present invention NLD method can run at a lower temperature than CVD method and still offers acceptable quality film because it is possible to modify the deposited film at low temperature to obtain the desired film properties. This same advantage exists over CVD when comparing the same set of first precursors in each method. Since the deposition step in both NLD and CVD depends on the substrate temperature, a lower substrate temperature would offer a lower deposition rate, and a better controllability of the deposited film such as surface coverage.

[0049] Another example is the densification of a deposited film. CVD method would deposit a complete film, then subject the whole film to a treatment such as annealing. Since the whole film is thick, the annealing would take a long time, and in some cases, certain limitation of diffusion could prevent the heat treatment from reaching the bottom of the deposited film. In contrast, the NLD method offers the cyclic sequential method of depositing and heat-treating a small fraction of the whole film. The whole film will be deposited a number of time, each time with only a fraction of the thickness. Since the fraction of the thickness is much thinner than the whole film thickness, the heat treatment would be short and effective. The number of cycles can be chosen to optimize the film quality or the short process time.

[0050] Another example is the capability of composition modification of the deposited film such as the carbon removal treatment of a carbon-containing deposited film. CVD method would deposit a complete film containing a certain amount of carbon, then subject the whole film to an energetic species such as plasma hydrogen to react with the carbon to remove the carbon from the deposited film. To reach a thick film, the energy needed for the energetic species would be very high, and in many cases would be impractical and potentially cause damage to the deposited film or the underlying substrate. In contrast, the NLD method offers the cyclic sequential method of depositing and carbon removal treatment of a small fraction of the whole film. Since the film to be treated is much thinner, and can be chosen as thin as one desires, the energy of the energetic species can be low and within the range of practicality, to remove the carbon and not damage the deposited film or the underlying substrate.

[0051] Another example is the avoidance of gas phase reaction such as the deposition of TiN using TDMAT metal organic precursor with NH_3. CVD method would be impractical since TDMAT would react with NH_3 in gas phase to create particles and roughen the deposited film. A CVD deposition of the whole film using TDMAT and then subjected the deposited film with NH_3 would not be possible to treat the whole film thickness. In contrast, the present invention NLD method offers the cyclic sequential method of depositing using TDMAT and NH_3 treatment of a small fraction of the whole film. With a deposited film thickness of TDMAT of less than a few nanometers (1-2 nm), the treatment of NH_3 would be effective, and only the cyclic sequential method of NLD would be able to provide. Similarly results can be obtained from TDEAT, TMEAT for titanium organic metal precursors, PDMAT, PDEAT for tantalum organic metal precursors, other organic metal precursors such as copper hexafluoroacetylacetonate trimethylvinylsilane ("Cu(hfac)TMVS"), inorganic precursors such as copper hfac (I), copper hfac (II), copper iodine, copper chloride, titanium chloride together with plasma treatment of N_2, H_2, Ar, He, or NH_3.

[0052] Another example is the modification of the property of the deposited film such as the deposition of a oxygen-rich film, a nitrogen-rich film, an oxy-nitride film, or a metal-rich film. To vary the content of any component in a deposited film such as oxygen, the CVD method would require the adjustment of all the precursor components. This is not an easy task since the incorporation of an element is not directly proportional to its presence in the precursor vapor form. Many times it is not even possible to modify the resulting film components since CVD is a product of a chemical reaction, and any excess precursors would not participate in the reaction. In contrast, the present invention NLD method offers the cyclic sequential method of depositing and treatment of a small fraction of the whole film. The treatment step is a separate step and can be designed to achieve the desired results. If an oxygen-rich film is desired, a energetic oxygen treatment step such as a plasma oxygen, or an ozone flow, could incorporate more oxygen into the deposited film. The incorporation can be done if the deposited film is thin enough, a condition only available in the present invention NLD method, not CVD. If an nitrogen-rich film is desired, a energetic nitrogen treatment step such as a plasma nitrogen, or an ammonia (NH_3) flow, could incorporate more nitrogen into the deposited film. If an oxy-nitride film is desired, a energetic oxygen treatment step could incorporate more oxygen into the deposited film of nitride, or a energetic nitrogen treatment step could incorporate more nitrogen into the deposited film of oxide.

[0053] Another example is the incorporation of impurity to modify the deposited film property such as, for example, copper doped aluminum film, carbon doped silicon dioxide film, or fluorine doped silicon dioxide film. For example, the electromigration resistance of pure aluminum is poor, but this resistance is much improved with the incorporation of a small amount of copper, typically less than a few percent. To incorporate copper, the CVD method would have to employ compatible precursors of aluminum and copper that can deposit a desired mixture. In contrast, the NLD method offers the cyclic sequential method of depositing a fraction of the aluminum film and incorporating copper into the film fraction during the treatment sequence. Since the deposition uses the aluminum precursors and the treatment uses the copper precursors, and these precursors are separately and sequentially introduced into the process chamber, the aluminum and copper precursors need not be compatible.

[0054] Another example is the deposition of multilayer films or nanolaminate films. Nanolaminate films are multilayer films but the different layers can be very thin, sometimes not complete layers, and sometimes even less than a monolayer. A CVD method would be impractical as it requires multiple process chambers and the ability to move a substrate between these chambers without incurring contamination and impurities. In contrast, the NLD method offers the cyclic sequential method of depositing a first layer film, and then depositing a second layer film during the treatment sequence. The first layer could be as thin as a fraction of a monolayer, or as thick desired, such as a few nanometers.

[0055] The NLD method also differs significantly from ALD method with a non self-limiting deposition step. The deposition step in the present invention NLD method is a function of substrate temperature and process time. The deposition/adsorption step in ALD method is a self-limiting step based on the saturation of precursor ligands on the substrate surface. Once the surface is saturated, the deposition/adsorption in ALD method stops and any excess precursor vapors have no further effect on the saturated surface. In other words, the deposition/adsorption step of ALD method is independent of time after reaching saturation. The ALD method also is less dependent on substrate temperature than CVD or NLD methods. Therefore, the present invention NLD method is different in many ways from ALD method.

[0056] Another example is that the non-self-limiting feature of the present invention NLD method allows the NLD method to share the precursors of CVD method, unlike ALD, which cannot use CVD precursors. The deposition step of the present invention NLD method is similar to the deposition step of the CVD method, with the possible exception of lower temperature. Therefore, the NLD method can use all the precursors of the CVD methods, including the newlydeveloped metal organic precursors or organic metal precursors (MOCVD precursors). In contrast, the precursor requirements of ALD are different because of the difference in the deposition mechanisms of ALD and NLD. ALD precursors must have a self-limiting effect so that the precursor is adsorbed on the substrate, up to a monolayer. Because of this self-limiting effect, only one monolayer or a sub-monolayer is deposited per cycle, and additional precursor will not be deposited on the grown layer even when excess precursor or additional time is supplied. The ALD precursors must readily adsorb at bonding sites on the deposited surface in a self-limiting mode. Once adsorbed, the precursor must react with the reactant to form the desired film. These requirements are different from CVD, where the precursors arrive at the substrate together and the film is deposited continuously from the reaction of the precursors at the substrate surface. Thus many useful CVD precursors are not viable as ALD precursors and vice-versa. And it is not trivial or obvious to select a precursor for the ALD method.

[0057] Another example of an advantage of the NLD method is the ease of incorporation of the enhancement of CVD technology, such as plasma technology and rapid thermal processing technology. By sharing precursors with CVD, the NLD method also can share all the advancement of CVD without much modification. A plasma deposition step in NLD can be designed and tested quickly because of the available knowledge of the CVD method.

[0058] Another example is the substrate surface preparation. This is a consequence of the different deposition mechanisms of NLD and ALD. In ALD, the substrate and substrate preparation are very critical and are a part of the deposition process, since different surfaces and surface preparations will lead to different film quality and properties. In contrast, in NLD, a similar deposition process occurs with different surface preparations or different surfaces because the basic mechanism is the deposition step, depending only on precursor reaction and the energy supplied, and depending little on the substrate surface. The only dependence of NLD on the substrate surfaces is the nucleation time, since different surfaces have different time for the precursors to nucleate and start depositing. This characteristic is observed in our laboratory when we deposit TiN using NLD process on different substrates: a silicon dioxide substrate, an organic polymer substrate, and a porous dielectric substrate. The TiN films on these three different substrates have similar film quality and properties, and only differ in thickness, due to the difference in nucleation times on different surfaces. Deposition of epitaxial films also requires intensive preparation of the substrate so that the first layer of atoms deposited grows epitaxially, or in an ordered arrangement from the substrate crystal. NLD process of non-epitaxial film allows conformal deposition or highly uniform coverage of a thin film over the vias and trenches, and especially high aspect ratio structures in semiconductor devices.

[0059] Another example is the ability to use MOCVD precursors in NLD. The MOCVD precursors contain a significant amount of carbon due to its organic content. The present invention NLD process uses MOCVD precursors with ease due to the deposition step using MOCVD precursors and the treatment step to remove any carbon left behind during the deposition step. An effective carbon removal step is the introduction of energetic hydrogen or nitrogen such as plasma hydrogen or nitrogen. In contrast, the use of MOCVD precursors in ALD method would demand significant research, and so far to the best of our knowledge, there is no commercially successful ALD process available using MOCVD precursors.

[0060] Another example is the non-self-limiting feature of the present invention NLD method also allows the NLD method to adjust the thickness of the deposition step, or the treatment step, or both, to achieve a higher thickness per cycle. The ALD method is based on the saturation of ligands on the substrate surface, therefore the thickness per cycle is fixed and cannot be changed. In contrast, the thickness per cycle in the present invention NLD method is a function of process temperature and process time. The optimum thickness for NLD process is the largest thickness per cycle and still able to be treated during the treatment step. An NLD process deposits TiN using TDMAT precursor and plasma nitrogen treatment can have the thickness per cycle any where from less than one nanometer to a few nanometers. The ability to vary the thickness per cycle allows the NLD process to use less cycles for the same total film thickness, leading to a faster process time and offering higher throughput than ALD process.

[0061] Another example is that the non-self-limiting feature of the present invention NLD method also allows the NLD method to vary the individual thickness of the resulting film, such as a few thicker or thinner layers in the middle of the deposited film, which is not possible in ALD method. Some applications require a thick film where the film quality is only critical to the interface, the center portion of the film can be deposited with a very high thickness per cycle to increase the throughput while the beginning and the end of the deposition is much thinner per cycle to satisfy the requirement of high quality interfaces. This feature is not possible with ALD process, for which all the cycles having the same thickness per cycle.

[0062] Another example is the process temperature of a deposited film. The ALD process temperature is largely fixed by the chemical reactions between the ligands of the precursors, and therefore ALD method is insensitive to the substrate temperature. In contrast, the present invention NLD method can run at a slightly higher temperature than ALD to offer the deposition characteristics, meaning a process dependent on process temperature and time. Furthermore, the NLD process can run at a much higher temperature to provide a larger thickness per cycle. The variation in thickness per cycle of NLD process can be accomplished by changing the substrate temperature, where a higher temperature would result in a high deposition rate, leading to a larger thickness per cycle. The change in substrate temperature is probably best accomplished by rapid thermal processing using radiative heat transfer for fast response time. A resistive heated substrate could provide the baseline temperature, and a lamp heating would provide the increase in temperature needed for larger thickness per cycle.

[0063] Another example is that it is not essential to have a purging step between the deposition and the treatment in the present invention NLD method because it is possible that the precursors in both steps are compatible. In contrast, ALD method requires the purging step between these two steps because of the designed reaction at the substrate surface. The purging step in NLD method helps overall in the cyclic sequential deposition scheme where the incompatibility of the two sets of precursors could cause potential damage. In rare cases where the two sets of precursors are compatible, the purging step is not critical and can be reduced or eliminated to improve the throughput.

[0064] Another example is the controllability of surface coverage. ALD method has excellent conformality and surface coverage, meaning this method will provide a theoretically perfect coverage of any configuration, as long as there is a pathway to it. But ALD is not capable of turning off this feature, meaning the excellent surface coverage is a characteristics of the ALD method. In contrast, in the present invention NLD, the surface coverage characteristics can be modified. In general, because of the deposition step in NLD is based on CVD, the thinner the thickness per cycle in NLD is, the better the surface coverage is. This degree of control offers NLD an unexpected advantage in porous substrate. ALD deposition on an open-pored porous substrate will travel through all the pores and deposit everywhere, potentially shorting the circuit if the deposited film is conductive. In contrast, NLD method can deliver a very high deposition rate at the beginning of the deposition cycle, effectively sealing off the open pores before starting deposition of a high quality thin film. By turning off the surface coverage feature, the degree of penetration of NLD into the porous material is significantly less than ALD method. Using this scheme, we have demonstrated a less penetration of the deposited film into the porous substrate. With further optimization, we believe that no penetration might be possible.

[0065] Another example of an advantage of NLD is the flexibility of design of the process chamber. The throughput of ALD is determined by the cycle time due to the independent of the thickness per cycle feature of ALD method. Therefore the chamber design in ALD is highly critical to achieve an acceptable throughput. ALD throughput depends strongly on many issues of chamber design, such as small chamber volume to ensure fast saturation and fast removal of precursors, fast switching valves to ensure quick response time of precursor on-off, uniform precursor delivery to ensure non-depletion effect of precursor. The fast response time requirement of ALD also puts a constraint on the timing requirement such as the synchronization of the precursor flow, the purging steps. In contrast, in the present invention NLD method, the chamber design issues are not as critical because of the potential higher thickness per cycle feature, leading to less number of cycles and higher throughput. Therefore a conventional CVD chamber with large volume, slow valve response time is adequate to perform NLD process. The NLD process could benefit from the chamber design of ALD, but NLD has the flexibility of trading some of the throughput for the simplicity of chamber design because the throughput of NLD without any chamber design consideration could be adequate for many applications. The advantage of the flexibility in chamber design is the ease of incorporate high density plasma into NLD process. High density plasma design requires a large chamber volume to equalize the energy of the charged and neutral particles due to high collision, and this requirement constraint contradicts with the small chamber volume requirement of ALD process, but acceptable with NLD process.

What is claimed is:

1. A deposition method to deposit a thin film comprising the steps of:
   a. introducing into a chamber a first plurality of precursors to deposit a first layer on a substrate in a non-self-limiting deposition process;
   b. purging the first precursors; and
   c. introducing a second different plurality of precursors that modify the deposited first layer in a modification process, wherein at least one precursor of the second plurality of precursors differs from the first plurality of precursors.

2. The method of claim 1, further comprising:
   d. purging the second precursors after step (c).

3. The method of claim 1, further comprising a plurality of the steps (a)-(c) until a desired film thickness is reached.

4. The method of claim 2, further comprising a plurality of the steps (a)-(d) until a desired film thickness is reached.

5. The method of claim 1, wherein the step (a) further comprises applying a plasma energy in the deposition process.

6. The method of claim 1, wherein the step (a) further comprises applying a thermal energy in the deposition process.

7. The method of claim 1, wherein the step (c) further comprises applying a plasma energy in the modification process.

8. The method of claim 1, wherein the step (c) further comprises applying a high density plasma energy in the modification process.

9. The method of claim 1, wherein the step (c) further comprises applying a high pressure plasma energy of 0.1 to 5 Torr in the modification process.

10. The method of claim 1, wherein the step (c) further comprises applying a thermal energy in the modification process.

11. The method of claim 1, wherein the step (c) further comprises applying a bias voltage in the modification process.

12. The method of claim 1, wherein the method further comprises selecting the first plurality of precursors in step (a) from the group consisting of CVD precursors.

13. The method of claim 1, wherein the method further comprises selecting the first plurality of precursors in step (a) from a group consisting of MOCVD precursors.

14. The method of claim 1, wherein the method further comprises selecting the second plurality of precursors in step (c) is selected from the group consisting of nitrogen, oxygen, hydrogen, ammonia, NF_3, silane, ozone and argon.

15. The method of claim 1, wherein the method further comprises selecting the the second plurality of precursors in step (c) from the group consisting of CVD precursors.

16. The method of claim 1, wherein the method further comprises selecting the second plurality of precursors in step (c) from the group consisting of MOCVD precursors.

17. The method of claim 1, wherein the method further comprises forming a non-epitaxial deposited thin film.

18. An improved method for thin film processing, the improvement comprising building a modified thin film without self-limiting surface adsorption.

19. An improved method for depositing a thin film wherein the improvement comprises depositing a first plurality of species of precursors in a first layer, purging the precursors, and subsequently depositing a second plurality of species of precursors in at least one subsequent layer on top of the first layer, wherein the second plurality of species of precursors has at least one precursor different from the first plurality of species of precursors.

20. An improved method for depositing a thin film wherein the improvement comprises: applying a non-self-limiting deposition process that is temperature-sensitive and time-dependent, and modifying a deposited layer with sequential deposition.

21. A deposition method to deposit a thin film comprising the steps of:
    a. introducing into a chamber a first plurality of precursors to deposit a first layer on a substrate in a non-self-limiting deposition process;

b. displacing the first plurality of precursors out of the chamber with a non-reacting gas; and
c. introducing a second different plurality of precursors that modify the characteristics of the deposited first layer, wherein at least one precursor of the second plurality of precursors differs from the first plurality of precursors.

22. The method of claim 21 wherein the method further comprises combining step (b) with purging the first plurality of precursors from the chamber.

23. An improved method for depositing a thin film wherein the improvement comprises modifying deposited layers with subsequent deposited layers.

24. The method of claim 1 wherein the introducing steps (a) and (c) further comprise using liquid injection for liquid precursors.

25. The method of claim 1 wherein the introducing steps (a) and (c) further comprise using vapor draw for liquid precursors.

26. The method of claim 1 wherein the introducing steps (a) and (c) further comprise using a bubbler for liquid precursors.

27. The method of claim 1 wherein the step (a) further comprises applying a light energy in the deposition process.

28. A deposition method to deposit a layer comprising the steps of:

a. introducing into a chamber a first plurality of precursors to deposit a first layer on a substrate in a non-self-limiting deposition process;
b. purging the first precursors; and
c. introducing a second different plurality of precursors that modify the deposited first layer in a modification process, wherein at least one precursor of the second plurality of precursors differs from the first plurality of precursors.

29. A deposition method to deposit a thin film comprising the steps of:

a. introducing into a chamber a first plurality of precursors to deposit a first layer on a substrate in a non-self-limiting deposition process;
b. displacing the first plurality of precursors out of the chamber with a non-reacting gas while maintaining chamber pressure;
c. introducing a second different plurality of precursors that modify the characteristics of the deposited first layer, wherein at least one precursor of the second plurality of precursors differs from the first plurality of precursors; and
d. purging the second plurality of precursors from the chamber.

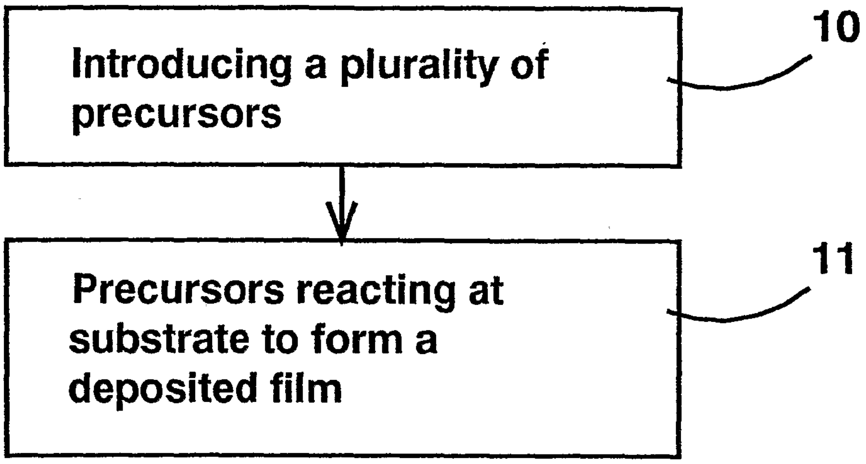

Fig. 1 (Prior Art)

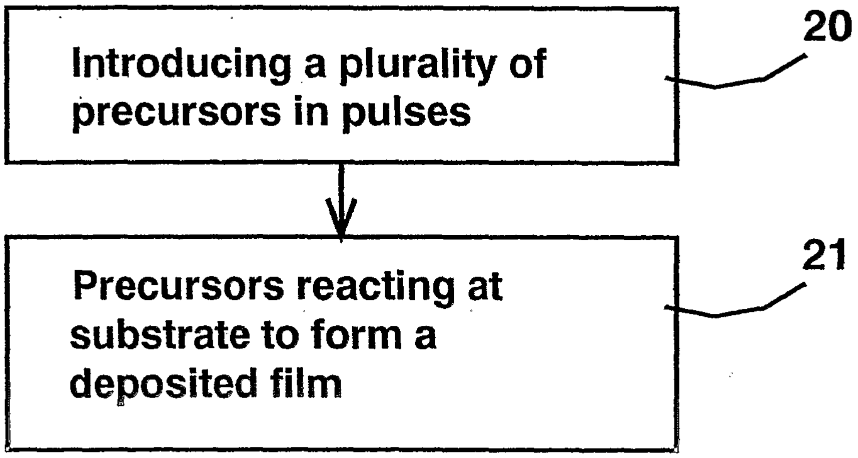

Fig. 2 (Prior Art)

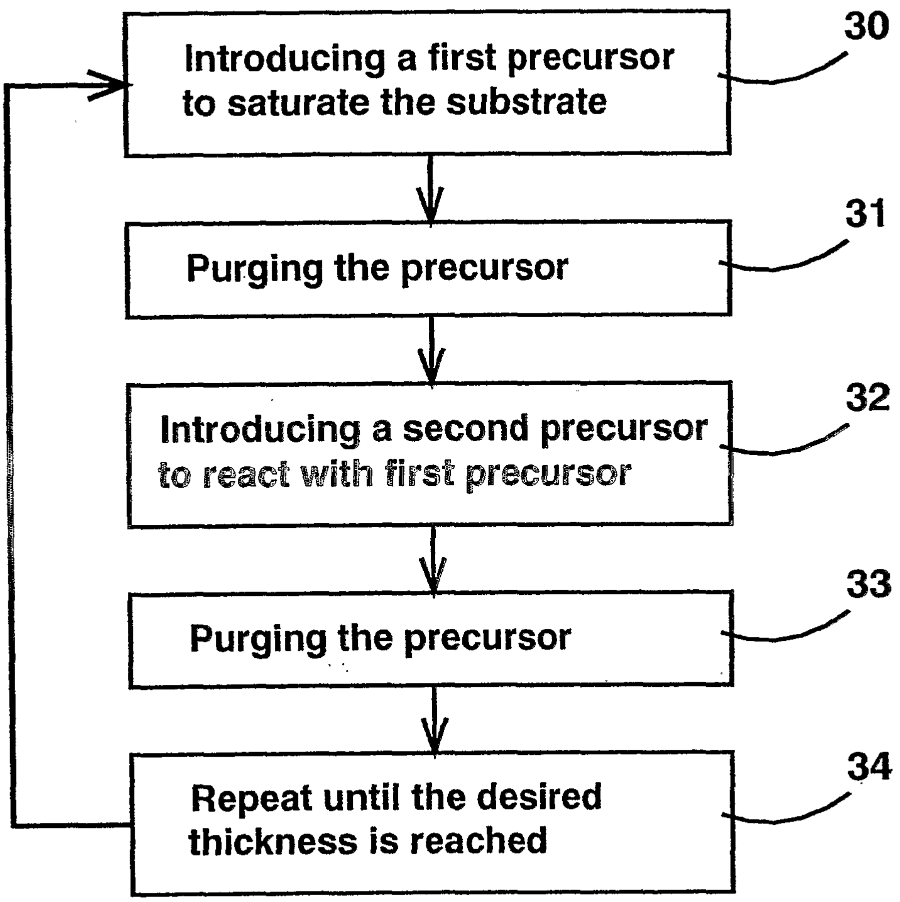

Fig. 3 (Prior Art)

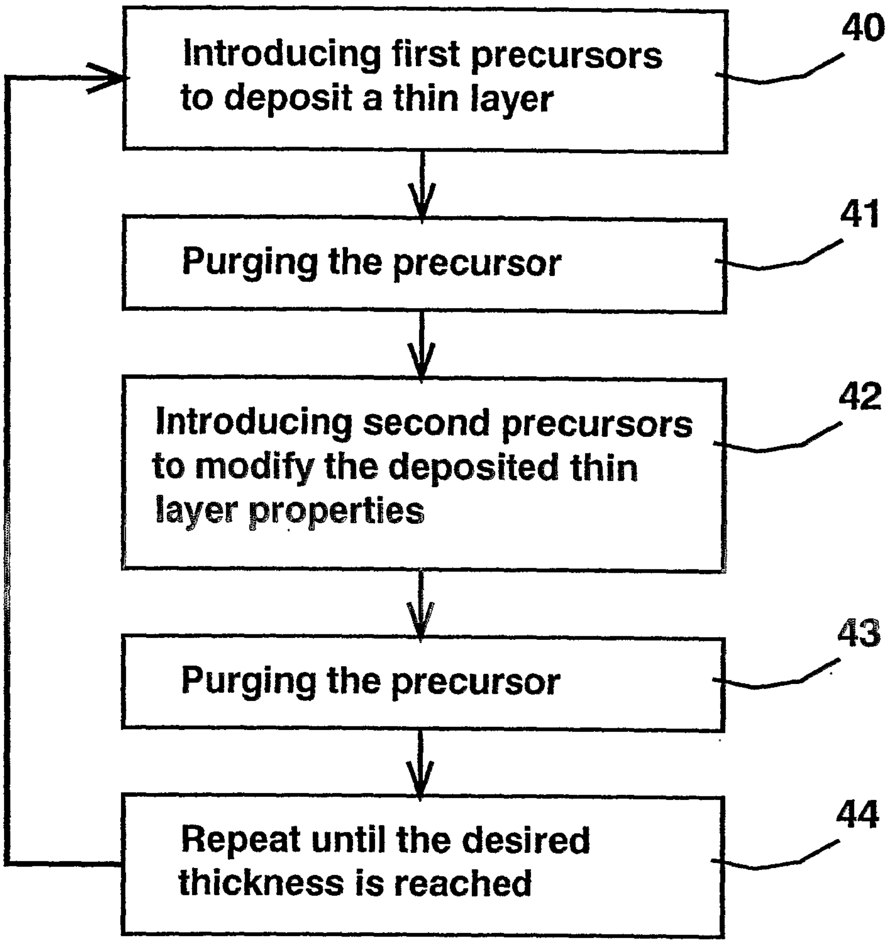
Introducing first precursors to deposit a thin layer
40
Purging the precursor
41
Introducing second precursors to modify the deposited thin layer properties
42
Purging the precursor
43
Repeat until the desired thickness is reached
44

Fig. 4