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(54) Title: IMPROVED DUAL DAMASCENE INTEGRATION STRUCTURES AND METHOD OF FORMING IMPROVED DUAL DAMASCENE INTEGRATION STRUCTURES

(57) Abstract: Methods for forming a dual damascene dielectric structure in a porous ultra-low-k (ULK) dielectric material by using gas-cluster ion-beam processing are disclosed. These methods minimize hard-mask layers during dual damascene ULK processing and eliminate hard-masks in the final ULK dual damascene structure. Methods for gas-cluster ion-beam etching, densification, pore sealing and ashing are described that allow simultaneous removal of material and densification of the ULK interfaces. A novel ULK dual damascene structure is disclosed with densified interfaces and no hard-masks.

IMPROVED DUAL DAMASCENE INTEGRATION STRUCTURES AND METHOD OF FORMING IMPROVED DUAL DAMASCENE INTEGRATION STRUCTURES

Field of the Invention

This invention relates generally to improved dual damascene integration structures for semiconductor integrated circuits utilizing low dielectric constant (low-k) dielectrics, and to methods of forming such structures using low-k dielectrics and the application of gas-cluster ion-beam processing.

Background of the Invention

The semiconductor industry has had tremendous success in delivering ever more cost effective chips to market through the use of scaling. However, while scaling works well in device or front end of semiconductor processing, device wiring is not amenable to scaling and results in degraded interconnect resistance and/or capacitance. To alleviate this problem, the industry has been migrating to the use of a lower resistance conductor (copper) and is also introducing lower-k insulators to reduce capacitance. Newly developed insulators in the ultra-low-k (ULK) range (k< 2.5) are generally characterized by a great deal of porosity (*e.g.*, 30-50%.) These materials are extremely difficult to integrate since they are susceptible to contamination from other wet chemicals and gases.

Conventional dual damascene ULK integration schemes rely on a series of higher-k hard-mask films to protect the surface of the porous and fragile ULK films. The two most widely used process sequences are the "via first" scheme and the conventional "dual hard-mask".

Figures 2A-2F show schematics illustrating in-process structures (identified as **300A-300F**) resulting after each step in a conventional "via first" dual damascene ULK integration process. The "via first" process begins with deposition of a sequence of insulator films over

the previous metal wiring level (not shown in the figures.) As shown in **Fig. 2A**, this insulator stack **300A** is comprised of etch stop film **302**, ULK dielectric layer **304**, first hard-mask layer **306**, second hard-mask layer **308**, antireflective coating **310**, and photoresist layer **312**. The etch stop film **302** must have a reasonably low-k value and the ULK dielectric layer

5   **304** must have a high etch rate ratio with respect to the etch stop film **302**. If the prior (underlying) metal wiring layer is copper, then this etch stop film **302** must also be a Cu diffusion barrier. The most commonly used etch stop films for this application are Si_3N_4 and SiCN.

10   The first hard-mask layer **306** is intended to remain as part of the dual damascene structure after processing to protect the fragile, porous ULK dielectric layer **304** from the effects of a subsequent chemical mechanical polishing (CMP) step. The second hard-mask layer **308** is a material that provides oxidation resistance and enables photo rework through ash removal of the antireflective coating **310** and the photoresist layer **312**. Typical materials used for first

15   hard-mask layer **306** are SiCOH or SiC while SiO_2 and Si_3N_4 are typically used for second hard-mask layer **308**. The second hard-mask layer **308** is a sacrificial layer and is removed during subsequent CMP of the Cu and barrier materials.

As reflected by structure **300B** of **Fig 2B**, the photoresist layer **312** is then imaged in the

20   desired via pattern and then reactive ion etching (RIE) is used to transfer the pattern down through the antireflective coating **310**, hard-mask layers **306** and **308** and through the ULK dielectric layer **304** while stopping on the SiCN etch stop, thus forming via **324**. As depicted in **Fig 2C**, any remaining photoresist layer **312** and antireflective coating **310** are removed by plasma ashing with mixtures of oxygen and other gases to obtain structure **300C**. Another

25   prior art alternative is plasma ashing of the resist followed by solvent removal of the antireflective coating layers. RIE polymer on the via sidewalls **314** is traditionally removed by wet cleans. It has been shown that both the oxygen plasma ashing and wet clean processes, which were traditionally used with SiO_2 dielectrics, can damage the porous ULK

dielectric layer 304 materials and so are not optimal because they are detrimental to the

process and can reduce the reliability and performance of the circuits thus formed.

5   As shown in **Fig 2D**, antireflective coating and photoresist materials are next re-applied to the

patterned wafer to obtain structure **300D**. A bottom antireflective coating **316**, which will fill

the etched vias (via **324**, for example) and planarize the surface is applied first. A third hard-

mask layer **318** is then applied, which will allow photo rework, and this is followed by a

standard antireflective coating **320** and photoresist layer **322**. One prior art alternative to this

scheme is to completely remove and then re-apply all anti-reflective coating and photoresist

10   layers during each photo rework operation.

Fig. 2E shows the stack (structure **300E**) after imaging the photoresist layer **322** in a desired

trench pattern and after transferring through RIE the pattern down through the third hard-

mask layer **318**, bottom antireflective coating **316**, second hard-mask layer **308**, first hard-

15   mask layer **306** and partially into the ULK dielectric layer **304**, thus forming a trench **326**. It

should be noted that the bottom antireflective coating **316** material should have a slightly

faster RIE etch rate than the ULK dielectric layer **304** material or un-etched protrusions

"fences" will remain around the via periphery.

20   Now referring to **Fig. 2F**, RIE is used to remove any remaining photoresist layer **322**,

antireflective coating **320**, third hard-mask layer **318**, bottom antireflective layer **316**, and to

open the underlying etch stop film **302**, thus completing via **324** and obtaining structure

300F. It should again be noted that oxygen RIE processes and any needed wet cleans have

been shown to permeate and degrade the porous ULK dielectric layer **304** material, to the

25   detriment of the process and to the reduced reliability and performance of the circuits thus

formed.

Figures 3A -3G show schematics illustrating in-process structures **400A-400G**

corresponding to stages in the prior art conventional "dual hard-mask" dual damascene ULK

integration scheme, a second widely used formation process.

5   As shown in **Fig. 3A,** the "dual hard-mask" process begins with deposition of a sequence of

insulator films over the previous metal wiring level.   Similar to the "via first" scheme

discussed above, this "dual hard-mask" insulator stack (structure **400A**) is also comprised of

an etch stop film **402**, a ULK dielectric layer **404**, a first hard-mask layer **406**, second hard-

mask layer **408**, an antireflective coating **410**, and a photoresist layer **412**. The first hard-

10   mask layer **406** in this integration scheme is intended to remain as part of the dual damascene

structure after processing to protect the fragile, porous ULK dielectric layer **404** from the

effects of subsequent CMP. A RIE etching chemistry for which the second hard-mask layer

408 has a high etch rate with respect to that for the first hard-mask layer **406** must be used

initially and subsequently other chemistries must be applied for which the second hard-mask

15   layer **408** has a low etch rate with respect to the ULK dielectric layer **404**. The second hard-

mask layer **408** is a sacrificial layer and is removed during CMP of the Cu and barrier

materials.

      As shown in **Fig 3B**, the photoresist layer **412** is then imaged in the desired trench pattern

20   and RIE is used to transfer the pattern down through the antireflective coating **410** and second

hard-mask layer **408**, stopping at first hard-mask layer **406**, thus forming trench pattern **414**

in the second hard-mask layer **408** in structure **400B**.

      As reflected in structure **400C** depicted in **Fig 3C**, the remaining photoresist layer **412** and

25   antireflective coating **410** are either removed by plasma ashing with mixtures of oxygen and

other gases or alternatively by using wet solvents.

As shown in **Fig 3D**, antireflective coating **416** and photoresist layer **418** are next re-applied to the patterned wafer to obtain structure **400D**.

Fig. 3E shows resultant structure **400E** following imaging of the photoresist layer **418** in the
5   desired via pattern followed by RIE transfer of the pattern down through the antireflective coating **416**, second hard-mask layer **408**, first hard-mask layer **406**, and partially into the ULK dielectric layer **404**, forming partial via **420**. It should be noted that the antireflective coating **416** material should have a similar etch rate to the second hard-mask layer **408** during this process.

10

As shown in **Fig 3F**, an ashing or RIE process is then used to remove any remaining photoresist layer **418** and antireflective coating **416** from the workpiece to obtain structure **400F**.

15   The structure **400G** illustrated in **Fig 3G** shows that next a RIE process is used to extend the second hard-mask layer's trench pattern **414** through first hard-mask layer **406** and into the ULK dielectric layer **404**, forming trench **424**, while simultaneously completing the via etch and thus opening up the underlying etch stop film at the bottom of the completed via **422**. The second hard-mask layer **408** is partially consumed during this process and is intended to
20   be completely removed during the subsequent barrier and Cu CMP process. It should also be noted that since a portion of the via **422** is not protected by resist or a hard-mask during this RIE process, the via shape tends to become elongated and to develop a sloped region **426** as also shown in **Fig 3G**. A subsequent argon pre-clean process for the Cu barrier and seed layer tends to sputter material from this sloped region **426** into the bottom of the via **422**, which is
25   typically a copper metal layer, and causes contamination and reliability problems.

A problem common to both of these prior art integration schemes ("via first" and "dual hard-mask" is that RIE is subject to micro-loading effects that lead to poor control of trench depth

and shape and, therefore, poor control of the wiring resistance and capacitance. The inability
to definitively specify wiring resistance and capacitance to the design community has a
negative impact on chip performance.

5   Since RIE leaves the etched ULK dielectric surfaces as an open porous structure, these
interfaces are not compatible with the desire to use ALD or CVD techniques for the
subsequent barrier and seed layer processes.

In addition, both of these prior art integration schemes utilize multiple hard-masks for
10   processing which are complex and costly. The final insulator dual damascene structure also
retains a hard-mask layer which raises the effective k value of the insulator structure and also
serves as a focal point for leakage, delamination, and other potential reliability problems.

There are a number of problems shared by both of these integration schemes. First, the
15   resulting final structures produced by these processes retain one or more of the hard-mask
layers. This raises the effective k value of the insulator structure and is not desirable. There
is additional motivation to minimize the use of these hard-mask layers in that every additional
material interface is a potential source for electrical leakage, delamination, or other reliability
problems. Also, the etched surfaces of the trench and via structure are open to contamination
20   from subsequent process steps. For example conventional wet or dry stripping processes
have been shown to contaminate the ULK films. In addition, it is desirable to use chemical
vapor deposition (CVD) or atomic layer deposition (ALD) processes to deposit the barrier
film in subsequent processing steps. It has been shown that ALD and CVD processes
penetrate the porous RIE etched sidewalls and raise the k value of the ULK films. Finally,
25   conventional RIE is subject to seasoning and micro-loading effects that lead to a great deal of
variability in the shape and depth of the trench and, therefore, the wiring resistance and
capacitance. This inability to definitively specify wiring resistance and capacitance to the
semiconductor design community has a negative impact on chip performance.

Summary of the Invention

The present invention uses gas-cluster ion-beam (GCIB) processing and novel integration structures to solve many of the problems described above.

5

The use of cluster ion beams for processing surfaces is known in the art (see for example, US patent 5,814,194, Deguchi *et al.*, incorporated herein by reference.) For purposes of this discussion, gas-clusters are nano-sized aggregates of materials that are gaseous under conditions of standard temperature and pressure. Such gas-clusters typically are comprised

10   of aggregates of from a few to several thousand molecules loosely bound to form the cluster. The clusters can be ionized by electron bombardment or other means, permitting them to be formed into directed beams of controllable energy. Such ions each typically carry positive charges of $q \cdot e$ (where e is the electronic charge and q is an integer of from one to several representing the charge state of the cluster ion). Non-ionized clusters may also exist within a

15   cluster ion beam. The larger sized cluster ions are often the most useful because of their ability to carry substantial energy per cluster ion, while yet having only modest average energy per molecule of from a fraction of an electron volt to a few tens of electron volts. The clusters disintegrate on impact, with each individual molecule carrying only a small fraction of the total cluster ion energy. Consequently, the impact effects of large cluster ions are

20   substantial, but are limited to a very shallow surface region. This makes cluster ions effective for a variety of surface modification processes, without the tendency to produce deeper subsurface damage characteristic of conventional monomer ion beam processing.

Apparatus for creation of and acceleration of such GCIBs are described in the reference (US

25   5,814,194) previously cited. Presently available cluster ion sources produce clusters ions having a wide distribution of sizes, N, up to 5000 or more (where N = the number of molecules in each cluster ion - in the case of monatomic gases like argon, an atom of the monatomic gas will be referred to herein as a molecule and an ionized atom of such a monatomic gas will be referred to as a molecular ion - or simply a monomer ion.) Many useful

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surface processing effects can be achieved by bombarding surfaces with GCIBs. These processing effects include, but are not necessarily limited to, cleaning, smoothing, etching, doping, and film formation or growth.

5   It is an objective of this invention to provide methods of GCIB processing of low-k dielectric materials to form dual damascene integration structures that minimize the requirement to use hard-masks.

It is another objective of this invention to provide methods of GCIB processing of low-k
10   dielectric materials to form dual damascene integration structures that include no hard-masks in the final etched structure.

It is a further objective of this invention to provide methods of densifying and sealing all etched surfaces to reduce their susceptibility to contamination from subsequent processes.

15

It is a still further objective of this invention to provide better control over etched trench depths and shapes and resultant interconnection resistance and capacitance.

It is still another objective of this invention to provide improved articles in the form of ULK
20   integration structures with a reduced number, or even no hard-mask uses in the dual damascene formation process and fewer to no hard-masks in the final etched structures.

Brief Description of the Figures

For a better understanding of the present invention, together with other and further objects
25   thereof, reference is made to the accompanying drawings and detailed description, wherein:

Figure 1 is a schematic showing the basic elements of a prior art GCIB processing apparatus;

Figures 2A-2F show schematics illustrating stages in the prior art conventional "via first" dual damascene ULK integration scheme;

Figures 3A-3G show schematics illustrating stages in the prior art conventional "dual hard-mask" dual damascene ULK integration scheme;

5   Figures 4A-4H show schematics illustrating an integration structure for a first embodiment of the invention and for explaining a first method of the invention; and

Figures 5A-5G show schematics illustrating an integration structure for a second embodiment of the invention and for explaining a second method of the invention.

10   **Detailed Description of Certain Preferred Embodiments of the Invention**

Figure 1 shows a schematic of the basic elements of a typical configuration for a GCIB processing apparatus **100** which may be described as follows: a vacuum vessel **102** is divided into three communicating chambers, a source chamber **104**, an ionization/acceleration chamber **106**, and a processing chamber **108**. The three chambers are evacuated to suitable operating

15   pressures by vacuum pumping systems **146a, 146b,** and **146c,** respectively. A condensable source gas **112** (for example argon or N_2) stored in a gas storage cylinder **111** is admitted under pressure through gas metering valve **113** and gas feed tube **114** into stagnation chamber **116** and is ejected into the substantially lower pressure vacuum through a properly shaped nozzle **110**. A supersonic gas jet **118** results. Cooling, which results from the expansion in

20   the jet, causes a portion of the gas jet **118** to condense into clusters, each comprising from several to several thousand weakly bound atoms or molecules. A gas skimmer aperture **120** partially separates the gas molecules that have not condensed into a cluster jet from the cluster jet so as to minimize pressure in the downstream regions where such higher pressures would be detrimental (e.g., ionizer **122**, high voltage electrodes **126**, and processing chamber

25   **108**). Suitable condensable source gases **112** include, but are not necessarily limited to argon, nitrogen, carbon dioxide, oxygen, and other gases and mixtures thereof.

After the supersonic gas jet 118 containing gas-clusters has been formed, the clusters are ionized in an ionizer 122. The ionizer 122 is typically an electron impact ionizer that produces thermoelectrons from one or more incandescent filaments 124 and accelerates and directs the electrons causing them to collide with the gas-clusters in the gas jet 118, where the

5   jet passes through the ionizer 122. The electron impact ejects electrons from the clusters, causing a portion the clusters to become positively ionized. Some clusters may have more than one electron ejected and may become multiply ionized. A set of suitably biased high voltage electrodes 126 extracts the cluster ions from the ionizer, forming a beam, and then accelerates them to a desired energy (typically with acceleration potentials of from several

10   hundred V to several tens of kV) and focuses them to form a GCIB 128. Filament power supply 136 provides filament voltage V_f to heat the ionizer filament 124. Anode power supply 134 provides anode voltage V_A to accelerate thermoelectrons emitted from filament 124 to cause them to irradiate the cluster containing gas jet 118 to produce ions. Extraction power supply 138 provides extraction voltage V_E to bias a high voltage electrode to extract

15   ions from the ionizing region of ionizer 122 and to form a GCIB 128. Accelerator power supply 140 provides acceleration voltage V_{Acc} to bias a high voltage electrode with respect to the ionizer 122 so as to result in a total GCIB acceleration potential equal to V_{Acc} . One or more lens power supplies (142 and 144 shown for example) may be provided to bias high voltage electrodes with focusing voltages (V_{L1} and V_{L2} for example) to focus the GCIB 128.

20

A workpiece 152, which may be a semiconductor wafer or other workpiece to be processed by GCIB processing, is held on a workpiece holder 150, which can be disposed in the path of the GCIB 128. Since most applications contemplate the processing of large workpieces with spatially uniform results, a scanning system is desirable to uniformly scan the GCIB 128

25   across large areas to produce spatially homogeneous results.

The GCIB 128 is stationary, has a GCIB axis 129, and the workpiece 152 is mechanically scanned through the GCIB 128 to distribute the effects of the GCIB 128 over a surface of the workpiece 152.

An X-scan actuator 202 provides linear motion of the workpiece holder 150 in the direction of X-scan motion 208 (into and out of the plane of the paper). A Y-scan actuator 204 provides linear motion of the workpiece holder 150 in the direction of Y-scan motion 210,

5   which is typically orthogonal to the X-scan motion 208. The combination of X-scanning and Y-scanning motions moves the workpiece 152, held by the workpiece holder 150 in a raster-like scanning motion through GCIB 128 to cause a uniform (or otherwise programmed) irradiation of a surface of the workpiece 152 by the GCIB 128 for processing of the workpiece 152. The workpiece holder 150 disposes the workpiece 152 at an angle with

10   respect to the axis of the GCIB 128 so that the GCIB 128 has an angle of beam incidence 206 with respect to the workpiece 152 surface. The angle of beam incidence 206 may be any suitable angle, but is typically 90 degrees or near 90 degrees. During Y-scanning, the workpiece 152 and the workpiece holder 150 move from the position shown to the alternate position "A" indicated by the designators 152A and 150A respectively. Notice that in

15   moving between the two positions, the workpiece 152 is scanned through the GCIB 128 and in both extreme positions, is moved completely out of the path of the GCIB 128 (over-scanned). Though not shown explicitly in **Figure 1**, similar scanning and over-scan is performed in the (typically) orthogonal X-scan motion 208 direction (in and out of the plane of the paper).

20

A beam current sensor 218 is disposed beyond the workpiece holder 150 in the path of the GCIB 128 so as to intercept a sample of the GCIB 128 when the workpiece holder 150 is scanned out of the path of the GCIB 128. The beam current sensor 218 is typically a faraday cup or the like, closed except for a beam-entry opening, and is typically affixed to the wall of

25   the vacuum vessel 102 with an electrically insulating mount 212.

A controller 220, which may be a microcomputer based controller connects to the X-scan actuator 202 and the Y-scan actuator 204 through electrical cable 216 and controls the X-scan actuator 202 and the Y-scan actuator 204 so as to place the workpiece 152 into or out of the

GCIB 128 and to scan the workpiece 152 uniformly relative to the GCIB 128 to achieve

desired processing of the workpiece 152 by the GCIB 128. Controller 220 receives the

sampled beam current collected by the beam current sensor 218 by way of lead 214 and

thereby monitors the GCIB and controls the GCIB dose received by the workpiece 152 by

5   removing the workpiece 152 from the GCIB 128 when a predetermined desired dose has been

delivered.

For use in the present invention, the inventors have developed GCIB processes useful at

several stages of semiconductor integration. These include processes for etching, for ashing

10 photoresists and the like, and for densifying and pore sealing of porous ULK dielectrics.

Table 1					
GCIB Processing Parameters for Etching Processes (all Values are Approximations)					
Some Useful Gasses	Typical Gas	Range of Gas Flow (SCCM)	Typical Gas Flow (SCCM)	V_{ACC} Range (kV)	Typical V_{ACC} (kV)
O_2 and Fluorine-containing gases such as CF_4, CHF_3, C_2F_2, SF_6, NF_3, and Mixtures of fluorine-containing gases with O_2, for example 1-10%NF_3 in 90-99%O_2	5%NF_3 in 95%O_2	200 - 2000	500	10 - 80	30

Although several useful gasses and gas mixtures are listed in **Table 1**, many other gasses and

mixtures are also useful in different etching situations, and practice of the invention is not

15 necessarily limited to use of the preferred gasses and conditions specified in **Table 1**.

Optimal gas flow is dependent on the characteristics of the GCIB processing system. The

gas flow values listed in **Table 1** are optimized for use in either the commercially available

nFusion™ model GCIB200 processing system, or the nFusion™ model GCIB300 processing

system, both manufactured and offered commercially by Epion Corporation (Billerica, MA.)

The GCIB dose required for etching is determined by the material and thickness etched, but typical doses are on the order of 1 x 10^{15} ions/cm$_2$. It should be noted that often it is desirable to etch two or more materials simultaneously and to have a controllable ratio of etch rate for each of the materials. In such cases, mixtures of gases are particularly useful and by

5   controlling the ratio of gases in the mixture, the differential etch rates for different materials can be controlled. As an example, the 1-10% NF$_3$ in 90 – 99% O$_2$ gas mixture suggested in Table 1, is useful for controlling differential etch rates by varying the gas mixture.

Table 2					
GCIB Processing Parameters for Ashing Processes (all Values are Approximations)					
Some Useful Gasses	Typical Gas	Range of Gas Flow (SCCM)	Typical Gas Flow (SCCM)	V$_{ACC}$ Range (kV)	Typical V$_{ACC}$ (kV)
O$_2$, N$_2$, He, H$_2$, Ar, and mixtures of these gases	N$_2$	200 - 2000	700	10 - 80	30

10   Although several useful gasses/mixtures are listed in Table 2, many other gasses and mixtures are also useful in different ashing situations, and practice of the invention is not necessarily limited to use of the preferred gasses and conditions specified in Table 2. Optimal gas flow is dependent on the characteristics of the GCIB processing system. The gas flow values listed in Table 2 are similarly optimized for use in either the commercially available

15   nFusion^{TM} model GCIB200 processing system, or the nFusion^{TM} model GCIB300 processing system. The GCIB dose required for ashing is determined by the material and thickness etched, but typical doses are on the order of 1 x 10^{15} ions/cm$_2$.

Table 3					
GCIB Processing Parameters for ULK Dielectric Surface Densification & Pore Sealing Processes (all Values are Approximations)					
Some Useful Gasses	Typical Gas	Range of Gas Flow (SCCM)	Typical Gas Flow (SCCM)	V$_{ACC}$ Range (kV)	Typical V$_{ACC}$ (kV)
O$_2$, Ar, N$_2$, CH$_4$ and mixtures of CH$_4$ with Ar	N$_2$	200 - 2000	700	2.5 – 20 for Ar and Ar mixtures 2.5-80 for O$_2$,	15

				N₂	30

Although several useful gasses/mixtures are listed in **Table 3**, many other gasses and mixtures are also useful in different ULK dielectric surface densification and pore sealing situations, and practice of the invention is not necessarily limited to use of the preferred gasses and

5   conditions specified in **Table 3**. Optimal gas flow is dependent on the characteristics of the GCIB processing system. The gas flow values listed in **Table 3** are similarly optimized for use in either the nFusion™ model GCIB200 model GCIB300 processing systems. The GCIB dose required for ULK dielectric surface densification and/or pore sealing is dependent on the material, but typical optimized doses are on the order of 1×10^{14} to 5×10^{14} ions/cm₂.

10   Doses higher than 5×10^{14} ions/cm² may be used, but saturation may occur and additional improvement is seldom achieved with higher doses. By controlling GCIB conditions (V_{ACC}, dose, gas, etc. – see **Table 3**) and depending on the ULK material employed, experimentally observed densified layer thicknesses range from less than about 50 Angstroms to more than about 350 Angstroms.

15

Figures 4A-4G illustrate in-process integration structures **500A-500G** resulting from inventive process steps in a first embodiment of the present invention, a method for fabricating the dual damascene integration structure **500H** shown in **Fig. 4H** incorporating porous ULK dielectrics. None of the suggested dimensions in any of the following

20   embodiments are intended to limit the invention in any manner to such embodiments.

Referring to **Fig. 4A**, a process in accordance with the first embodiment of the invention begins with deposition of a sequence of insulator films over the previous metal wiring level (not shown, but would appear below the stop film layer **502** in structure **500A**.) The

25   insulator stack is comprised of an etch stop film **502**, porous ULK dielectric layer **504** and a hard-mask layer **506**. The etch stop material has the same requirements as previously stated for the prior art processes and therefore is typically composed of a material such as Si_3N_4 or SiCN. The etch stop film **502** may have a thickness of about 35 nm. The porous ULK dielectric layer **504** may have a thickness (for example) of about 300 nm.

The hard-mask layer **506** in this integration scheme does not remain as part of the dual

damascene structure after processing. Therefore, relatively higher-k materials such as SiO_2 or

Si_3N_4 may be used for hard-mask layer **506** compared to what would be required in a

5   conventional integration scheme. Since SiO_2 or Si_3N_4 are also oxidation resistant, photo

rework is allowed. The hard-mask layer **506** may have a thickness (for example) of about 40

nm.

In addition to SiO_2 and Si_3N_4, other suitable hard mask materials include, but are not

10 necessarily limited to SiCOH, SiCN and SiC. Prior to formation of the hard-mask layer **506**,

the surface of the porous ULK dielectric layer **504** may be densified and pore-sealed by

GCIB processing (see **Table 3** for typical process parameters.)

As is illustrated in **Fig. 4B**, an antireflective coating **508** and a photoresist layer **510** of types

15 known in the art are applied to insulator stack **500B**. In most applications, the antireflective

coating **508** and photoresist layer **510** will both be employed, but there may be applications

wherein antireflective coating is not necessary. The antireflective coating **508** and photoresist

layer **510** are collectively referred to herein as a "masking material" layer, however the same

term could be applied, in such embodiments, to refer to a photoresist-only layer. The

20 antireflective coating **508** may be (for exemplary purposes) about 40 nm thick and the

photoresist layer **510** may be (for example) about 200 nm thick, measured from the upper

surface of coating **508**. The antireflective coating **508** may comprise (for example, not for

limitation) "AR 40 Anti-Reflectant" and the photoresist layer **510** may comprise (for

example, not for limitation) "Epic^{TM} 2210 ArF Photoresist", both materials supplied

25 commercially by Rohm and Haas Electronic Materials (Phoenix, AZ.)

As shown in **Fig. 4C**, the resist is then imaged in the desired via pattern and then RIE or

preferably GCIB etching (See **Table 1** for example process parameters) is used to transfer

the pattern down through the antireflective coating **508**, hard-mask layer **506**, and porous

ULK dielectric layer **504**, stopping on the etch stop film **502**, thus forming via **512** in

resultant structure **500C**.

5   As depicted in **Fig. 4D** the remaining photoresist layer **510** and antireflective coating **508** are

removed by conventional plasma or GCIB ashing with mixtures of oxygen and other gases

(See **Table 2** for example process parameters) to obtain structure **500D**. In the preferred

approach, the sidewalls of the etched via **512** in the porous ULK dielectric layer **504** are

cleaned and densified and rendered non-porous by the GCIB treatment (See **Table 3** for

10   example process parameters), thus avoiding the need for wet cleaning and avoiding the

opportunity for contamination that results from wet processing of porous dielectrics.

According to **Fig. 4E**, another masking material layer, comprised of optional bottom

antireflective coating **516** and photoresist layer **518** are next applied to the patterned wafer

15   (structure **500E**) as shown. Preferably the antireflective coating component of the masking

material layer fills the etched vias (via **512** for example) and planarizes the surface prior to

the application of photoresist. The bottom antireflective coating **516** and the photoresist

layer **518** may similarly be composed of the materials described above. Not including the via

filling depth, the bottom antireflective coating **516** material may be (for example) about 200

20   nm thick. The photoresist layer **518** may be (for example) about 200 nm thick. This

structure is significantly simpler than that of the prior art **Fig. 2D** and represents an

improvement since, in the preferred approach, GCIB ash removal of the photoresist and

antireflective coating can be used if photo rework capability is desired.

25   **Fig. 4F** shows a structure **500F** resulting from imaging the resist in the desired trench pattern

and then RIE or GCIB etch transferring the pattern down through the bottom antireflective

coating **516**, hard-mask layer **506**, and partially into the porous ULK dielectric layer **504**,

thus forming a trench **520**. The bottom antireflective coat **516** material should have a slightly

faster GCIB etch rate than the porous ULK dielectric layer **504** material to avoid un-etched

protrusions, "fences", remaining around the upper surface of the via 512 periphery. (See

Table 1 for example process parameters – note that the relative etch rates in the bottom

antireflective coat 516 and in the porous ULK dielectric layer 504 is controlled by setting the

ratio of NF_3 to O_2 in the gas mixture) As shown in Fig. 4G, an ashing process, preferably a

5   GCIB ashing process (See Table 3 for example process parameters) then removes any

remaining photoresist layer 518 and bottom antireflective coating 516 from the surface of the

workpiece 500G. This is followed by RIE or GCIB etching to remove the hard-mask layer

506 and to open up the underlying etch stop film 502 to complete the via 512 (See Table 1

for example process parameters.)

10

As shown in Fig. 4H, a final GCIB treatment (See Table 3 for example process parameters)

is then used to complete the densification and smoothing of all the exposed ULK dielectric

layer surfaces 522 to obtain the first embodiment of the improved dual damascence structure

500H.

15

Figures 5A-5G illustrate in-process structures 600A-600F and a final dual damascene

integration structure 600G using porous ULK dielectrics, formed in accordance with a second

embodiment of the present invention, and which is based on initial transfer of a trench

pattern into a hard-mask.

20

As shown in Fig. 5A, the process of the second embodiment begins with deposition of a

sequence of insulator films over the previous metal wiring level. This insulator stack 600A is

comprised of an etch stop film 602, a porous ULK dielectric layer 604 and a hard-mask layer

606. A masking material layer comprised of an optional antireflective coating 608 and

25   photoresist layer 610 are then applied to this insulator stack as also illustrated in this figure.

The etch stop material has the same requirements as previously stated for the prior art

processes and therefore is typically a material such as Si_3N_4 or SiCN. The etch stop film 602

may have a thickness (for example) of about 35 nm. The porous ULK dielectric layer 604

may have a thickness (for example) of about 300 nm. The hard-mask layer 606 in this

integration scheme does not remain as part of the dual damascene structure after processing. Therefore, relatively higher-k materials such as SiO_2 or Si_3N_4 may be used for hard-mask layer 606 compared to what would be required in a conventional integration scheme. Since SiO_2 or Si_3N_4 are also oxidation resistant, photo rework is allowed. The hard-mask layer 606 may

5   have a thickness (for example) of about 80 nm. This thickness is adjustable depending on the relative etch rates of the hard-mask to the ULK and underlying etch stop. In addition to SiO_2 and Si_3N_4, other suitable hard mask materials include, but are not necessarily limited to, SiCOH, SiCN and SiC. The antireflective coating 608 may be (for example) about 40 nm thick and the photoresist layer 610 may be (for example) about 200 nm thick. The

10 antireflective coating 608 and the photoresist layer 610 may similarly comprise (for example, not for limitation) the materials discussed above or other known materials. Note that, optionally, prior to formation of the hard-mask layer 606, the surface of the porous ULK dielectric layer 604 may be densified and pore-sealed by gas cluster ion beam processing (see Table 3 for typical process parameters).

15

Fig. 5B illustrates resultant structure 600B subsequent to imaging of the photoresist layer 610 in the desired trench pattern and then use of RIE or GCIB etching (See Table 1 for example process parameters) to transfer of the pattern down through the antireflective coating 608 and hard-mask layer 606, stopping after minimal etching of the porous ULK

20 dielectric layer 604, thus forming a trench pattern 612 in hard-mask layer 606.

As reflected by structure 600C depicted in Fig. 5C the remaining masking material layer is removed by a conventional plasma or GCIB ashing process with pure concentrations or mixes of oxygen, nitrogen, hydrogen, argon and other gases (See Table 2 for example process parameters) while simultaneously accomplishing densification of surface 614 of the porous

25 ULK dielectric layer 604.

Referring to Fig. 5D, another masking material layer composed of optional antireflective coating 616 and photoresist layer 618 are next applied to the patterned wafer (structure 600D) as shown. The antireflective coating 616 may comprise (for example, not for

limitation) "AR 40 Anti-Reflectant" and the photoresist layer **618** may comprise (for
example, not for limitation) "Epic™ 2210 ArF Photoresist."

As illustrated in **Fig 5E**, photoresist layer **618** is imaged in the desired via pattern and RIE or

5   GCIB etching is used to transfer the pattern down through the antireflective coating **616**, the
hard-mask layer **606**, and partially into the porous ULK dielectric layer **604**. The
antireflective coating material should have a similar etch rate to the hard-mask layer **606**
during this step (See **Table 1** for example process parameters – note that the relative etch
rates in the bottom antireflective coat **616** and in the porous ULK dielectric layer **604** is

10   controlled by setting the ratio of NF_3 to O_2 in the gas mixture.)

As shown in **Fig. 5F**, a conventional plasma or preferably GCIB ashing process (See **Table 2**
for example process parameters) is then used to remove any remaining material of the masking
material layer from the workpiece (structure **600F**.)

15

Referring to **Fig. 5G**, next a RIE or GCIB etch process is utilized which extends the hard-
mask layer **606** trench pattern **612** into the porous ULK dielectric layer **604**, thus forming
trench **624**, while simultaneously completing the via etch and opening up the underlying etch
stop at the bottom of the via, thus completing via **610** (See **Table 1** for example process

20   parameters). The hard-mask layer **606** is completely removed during this process. Finally,
another GCIB process is used to smooth and densify and to seal pores of all exposed ULK
surfaces **622** (See **Table 2** for example process parameters). Note that since GCIB etching is
highly directional, the sidewalls of the vias do not develop a shallow slope (they have
substantially no slope) as in a conventional RIE process (see **Fig. 3G** for illustration of this

25   problem in the prior art).

Importantly, utilizing GCIB processing eliminates the need for a hard-mask over a porous
ULK dielectric material, since the GCIB process can provide smoothing, densification, and

pore sealing of the etched ULK dielectric material. RIE removal of the hard-mask over ULK dielectric results in a roughened porous ULK dielectric surface. CMP removal of the hard-mask over ULK dielectric material can provide smoothing but no densification or pore sealing and therefore the associated wet chemistry degrades the porous ULK dielectric material.

5

Another benefit of this invention is that the number of hard-masks used in the formation of the dual damascene structure is minimized and hard-masks are eliminated in the final etched dual damascene structure. Therefore, the final dual damascene structure has a lower effective k and minimal interfaces that can be sources for leakage, delamination and other reliability

10   problems. The process causes densification and sealing of all porous etched ULK dielectric surfaces such that they are not susceptible to contamination from subsequent processes such CVD or ALD barrier processes. Finally, GCIB etching is not subject to micro-loading effects and therefore provides better control of the etched trench depth and shape such that more precise specification of resistance and capacitance can be made to the design community.

15

Although the invention has been described with respect to various embodiments, it should be realized this invention is also capable of a wide variety of further and other embodiments within the spirit of the invention.

20   It is claimed:

1.   A method of fabricating a dual damascene integrated structure, comprising the steps of:

forming a porous ultra-low k dielectric film on an underlying etch stop film;

forming a hard-mask layer on the porous ultra-low k dielectric film;

applying a first masking material layer on the hard-mask layer;

forming a via pattern in the first masking material layer;

transferring the via pattern in the first masking material layer through the
    hard-mask layer and through the porous ultra-low k dielectric film to
    the etch stop film so as to form therein one or more vias with exposed
    sidewalls;

forming a densified layer on the exposed sidewalls of the one or more vias in
    the porous ultra-low k dielectric film by gas cluster ion beam
    irradiation;

removing remnants of the first masking material layer;

applying a second masking material layer so as to form a layer on the hard-
    mask layer and to fill the one or more formed vias;

forming a trench pattern in the second masking material layer;

transferring the trench pattern in the second masking material layer through the
    hard-mask layer and at least partially through the porous ultra-low k
    dielectric film so as to form therein one or more trenches with exposed
    surfaces and sidewalls;

removing remnants of the second masking material layer;

forming a densified layer on the exposed surfaces and sidewalls of the one or
    more trenches; and

etching the structure by gas cluster ion beam irradiation to open the underlying
    etch stop layer in the one or more vias and to either partially or
    completely remove the hard-mask layer.

2.   The method of claim 1, wherein the transferring steps are accomplished using reactive ion etching.

3.   The method of claim 1, wherein the transferring steps are accomplished using gas cluster ion beam irradiation etching.

4.   The method of claim 3, wherein at least one of the transferring steps utilizes a gas cluster ion beam having gas cluster ions comprising a mixture of O_2 and a fluorine containing gas.

5.   The method of claim 1, further comprising the step of densifying the surface of the porous ultra-low k dielectric film by gas cluster ion beam irradiation prior to the forming a hard-mask layer step.

6.   The method of claim 5, wherein the gas cluster ion beam utilized in densifying the surface is comprised of gas cluster ions comprising one or more gases selected from the group consisting of O_2, Ar, N_2, CH_4 and mixtures of CH_4 with Ar.

7.   The method of claim 1, wherein the etch stop film is composed of Si_3N_4 or SiCN.

8.   The method of claim 1, wherein the hard-mask layer material is chosen from the group consisting of SiCOH, SiC, SiCN, Si_3N_4, and SiO_2.

9.   The method of claim 1, wherein one or more of the removing remnants steps is accomplished using gas cluster ion beam irradiation.

10.   The method of claim 1, wherein one or more of the removing remnants steps utilizes a gas cluster ion beam having gas cluster ions comprising one or more of the group of gases consisting of O_2, N_2, He, and H_2.

11.   The method of claim 1, wherein the first and second masking material layers are each comprised of a photoresist layer.

12.   The method of claim 11, wherein at least one of the first masking material layer or the second masking material layer further comprises an antireflective coating material layer.

13.   The method of claim 1, wherein the densified layers in the porous ultra-low k dielectric film have substantially sealed pores.

14.   The method of claim 1, wherein the step of transferring the via pattern is accomplished simultaneously with the forming a densified layer step through use of the same gas cluster ion beam irradiation.

15.   The method of claim 13, wherein the single gas cluster ion beam irradiation step utilizes a gas cluster ion beam comprising O_2.

16.   A method of fabricating a dual damascene integrated structure, comprising the steps of:

      forming a porous ultra-low k dielectric film on an underlying etch stop film;

      forming a hard-mask layer on the porous ultra-low k dielectric film;

      applying a first masking material layer on the hard-mask layer;

      forming a trench pattern in the first masking material layer;

      transferring the trench pattern in the first masking material layer through the hard-mask layer and minimally into the porous ultra-low k dielectric film so as to form therein one or more trench openings with exposed porous ultra-low k dielectric surfaces;

      forming a densified layer on the exposed porous ultra-low k dielectric surfaces of the one or more trench openings by gas cluster ion beam irradiation;

      removing remnants of the first masking material layer;

applying a second masking material layer on the hard-mask layer and the one

or more trench openings;

forming a via pattern in the second masking material layer;

transferring the via pattern in the second masking material layer at least

partially through the porous ultra-low k dielectric film so as to form

therein one or more via openings;

removing remnants of the second masking material layer;

etching the structure so as to deepen the one or more trench openings to

complete one or more trenches having exposed surfaces and sidewalls,

to deepen the one or more via openings to complete one or more vias

having exposed sidewalls, and to open the underlying etch stop layer in

the one or more vias;

removing the hard-mask layer; and

forming a densified layer on all exposed porous ultra-low k dielectric film

surfaces and sidewalls by gas cluster ion beam processing.

17.   The method of claim 16, wherein either step of transferring is accomplished using

reactive ion etching.

18.   The method of claim 16, wherein either step of transferring is accomplished using gas

cluster ion beam irradiation.

19.   The method of claim 16, wherein the transferring the via pattern step utilizes a gas

cluster ion beam having gas cluster ions comprising a mixture of O_2 and a fluorine

containing gas.

20.   The method of claim 16, further comprising the step of densifying the surface of the

porous ultra-low k dielectric film by gas cluster ion beam irradiation prior to the

forming a hard-mask layer step.

21.   The method of claim 20, wherein the gas cluster ion beam utilized in densifying the surface is comprised of gas cluster ions comprising one or more gases selected from the group consisting of O_2, Ar, N_2, CH_4 and mixtures of CH_4 with Ar.

5   22.   The method of claim 16, wherein the etch stop film comprises Si_3N_4 or SiCN.

23.   The method of claim 16, wherein the hard-mask layer is chosen from the group consisting of SiCOH, SiC, SiCN, Si_3N_4, and SiO_2.

10   24.   The method of claim 16, wherein one or more of the removing remnants steps is done by gas cluster ion beam irradiation.

25.   The method of claim 24 wherein at least one of the one or more removing remnants steps utilizes a gas cluster ion beam having gas cluster ions comprising one or more of

15   the group of gases consisting of O_2, N_2, He, and H_2.

25.   The method of claim 16, where in the first and second masking material layers each comprise a photoresist layer.

20   26.   The method of claim 25, wherein at least one of the first or the second masking material layer further comprises an antireflective coating material layer.

27.   The method of claim 16, wherein the step of transferring the trench pattern is accomplished simultaneously with the forming of a densified layer step through use of

25   the same gas cluster ion beam irradiation.

28.   The method of claim 27, wherein the single gas cluster ion beam irradiation step utilizes a gas cluster ion beam comprising O_2.

29.   A structure in which a dual damascene trench and via pattern is formed including a porous, ultra-low k dielectric material layer and an underlying etch stop material layer, wherein said porous, ultra-low k dielectric material layer has substantially densified, substantially non-porous surfaces and sidewalls.

5

30.   The structure of claim 29, wherein a hard-mask material covers the top surface of the porous ultra-low k dielectric material.

31.   The structure of claim 30, wherein the interface between the hard-mask material and the porous ultra-low k dielectric material is substantially densified and substantially non-porous ultra-low k dielectric material.

10

32.   The structure of claim 29, being essentially free of hard-mask material.

15   33.   The structure of claim 29, wherein the via sidewalls have substantially no slope.

34.   A method, comprising the steps of:

        forming a porous ultra-low k dielectric material layer; and

        etching at least a portion of said porous ultra-low k dielectric material layer by

20   exposing said portion to a gas clustered ion beam.

35.   The method of claim 34, wherein said etching forms at least one trench or via in said ultra-low k dielectric material layer having sidewalls with substantially no slope.

25   36.   A method of removing residual masking material from a semiconductor structure to which a pattern has been transferred via application of a masking material to the structure followed by imaging and etch, comprising the step of:

        irradiating the residual masking material with a gas cluster ion beam.

30
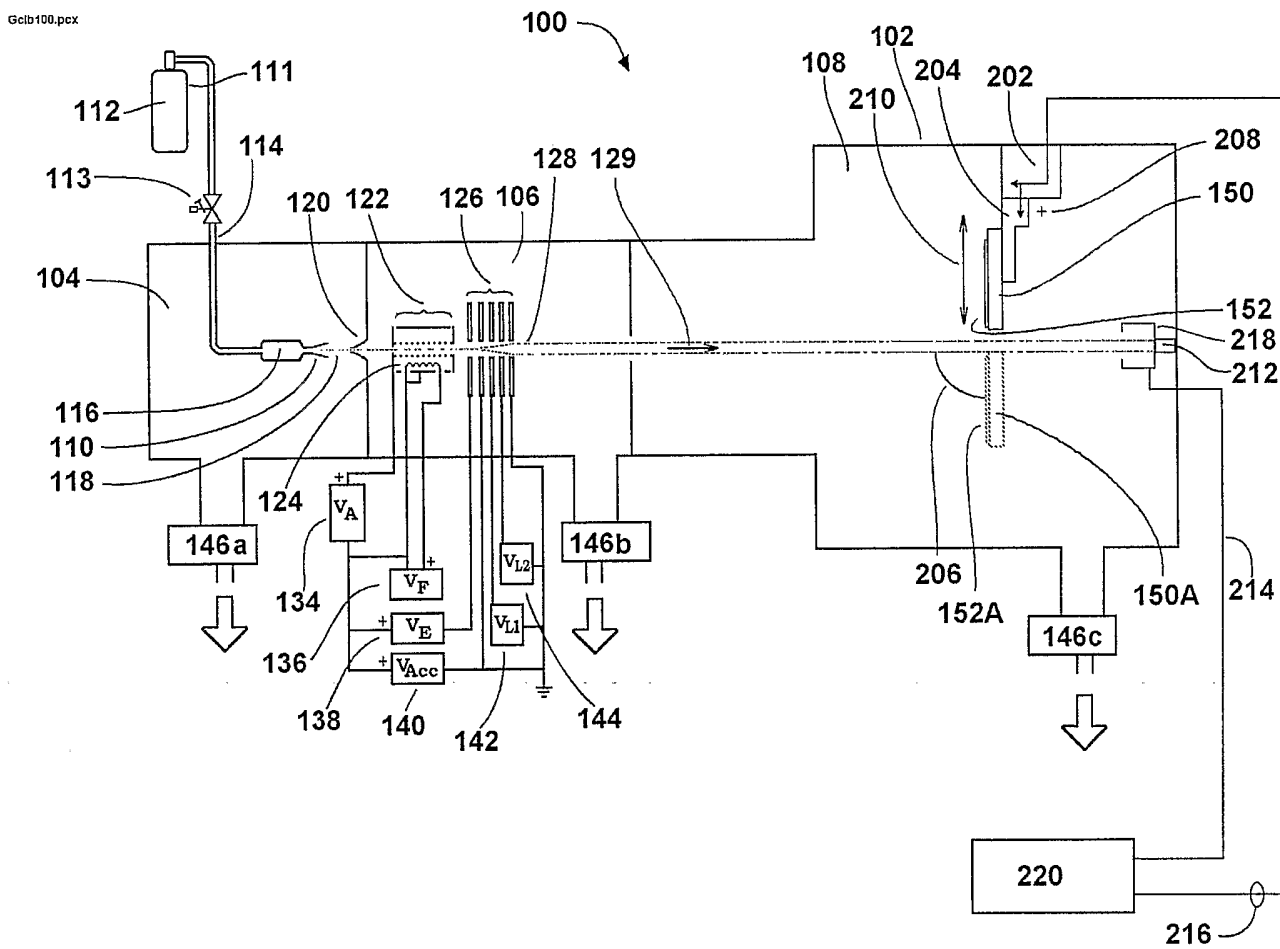
Gclb100.pcx

Figure 1 Prior Art.

300A

312
310
308
306
304
302

Figure 2A   Prior Art.

300B

324

312
310
308
306
304
302

Figure 2B   Prior Art.

300 C

314
308
306
304
302
324

Figure 2C Prior Art.

300 D

322
320
318
316
308
306
304
302
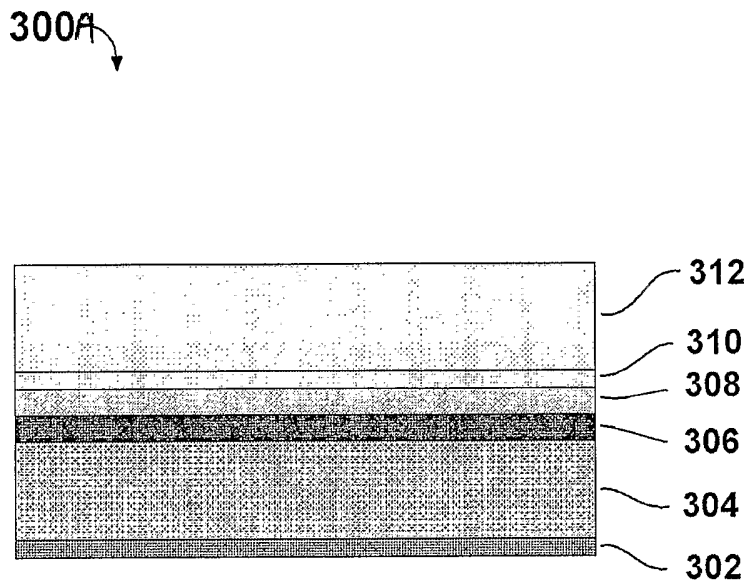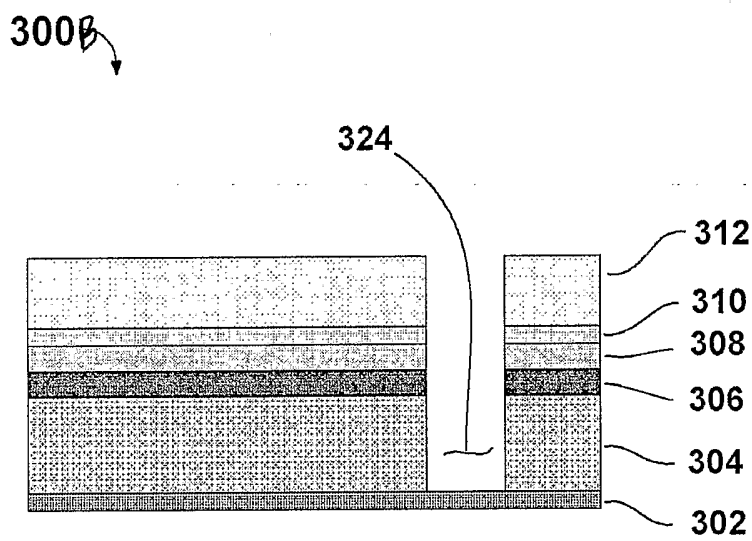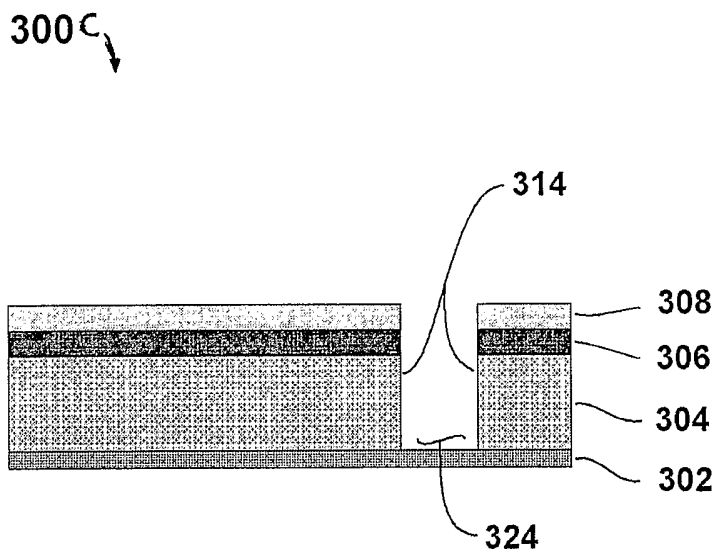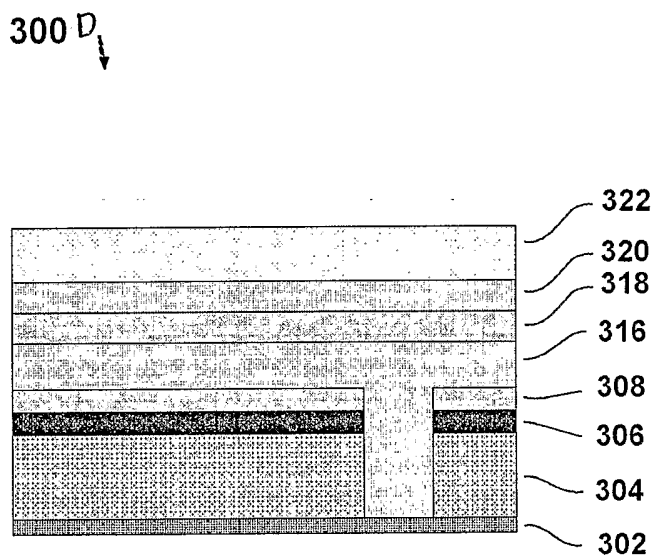
Figure 2D Prior Art.

300 E
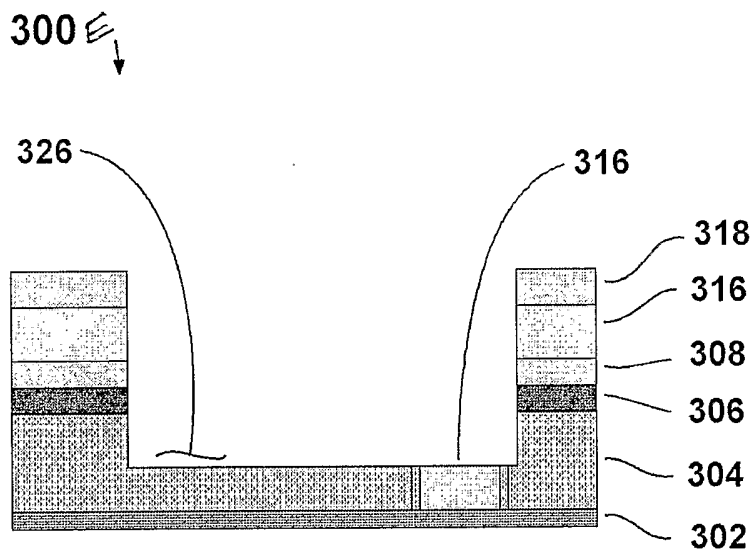
Figure 2E Prior Art.

300 F
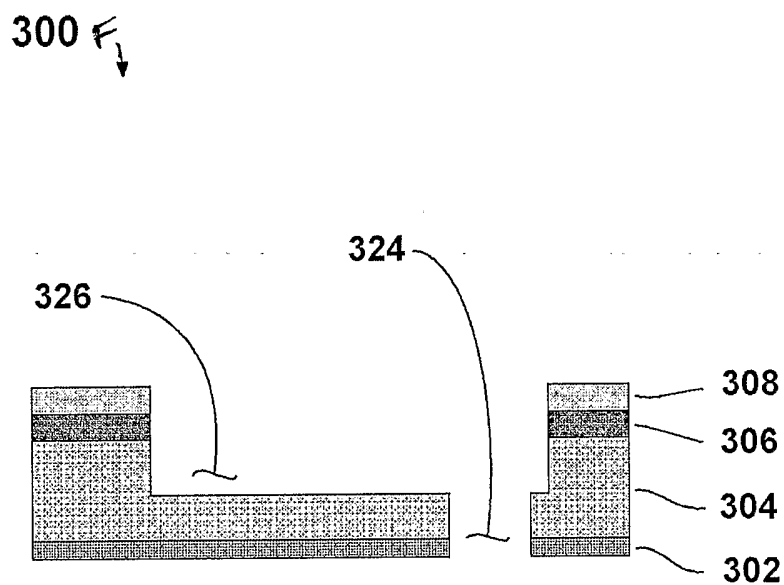
Figure 2F Prior Art.

400 A
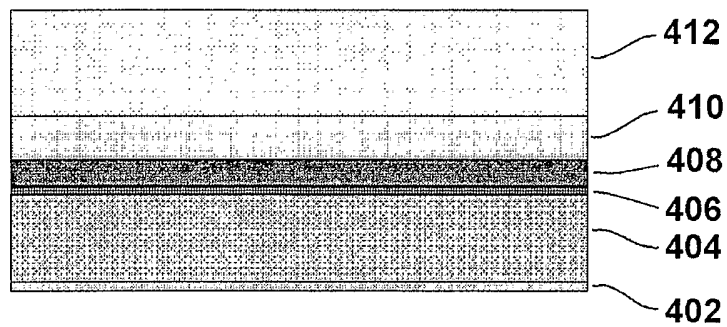
—412
—410
—408
—406
—404
—402

Figure 3A Prior Art.

400 B
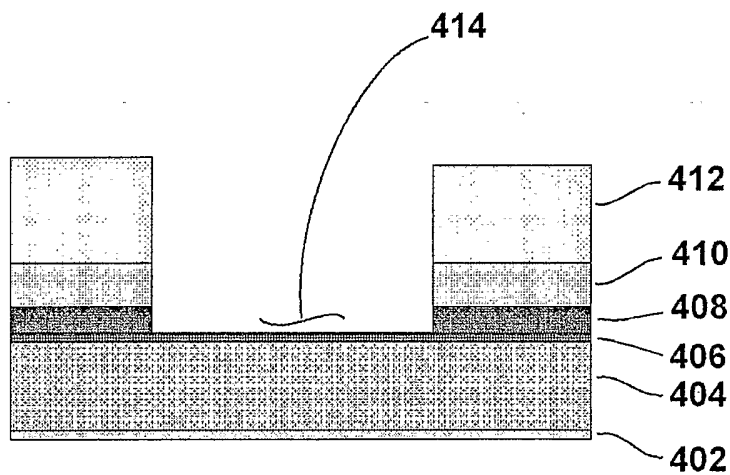
414

—412
—410
—408
—406
—404
—402

Figure 3B Prior Art.

400 C

414

408
406
404
402

Figure 3C Prior Art.

400 D

418
416
408
406
404
402

Figure 3D Prior Art.

400E

420

418
416
408
406
404

402

Figure 3E Prior Art.

400 F

414   420

408
406
404

402
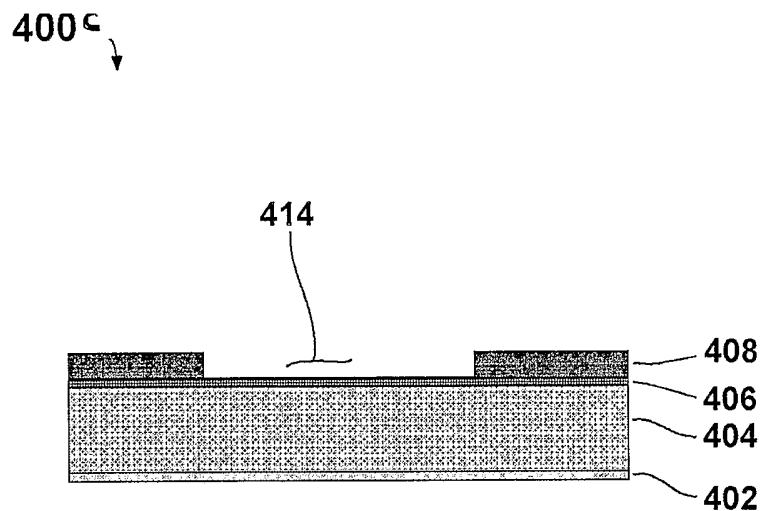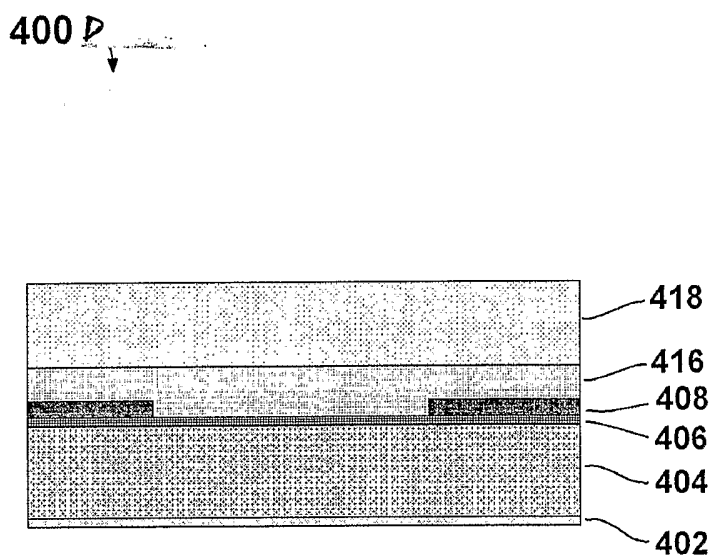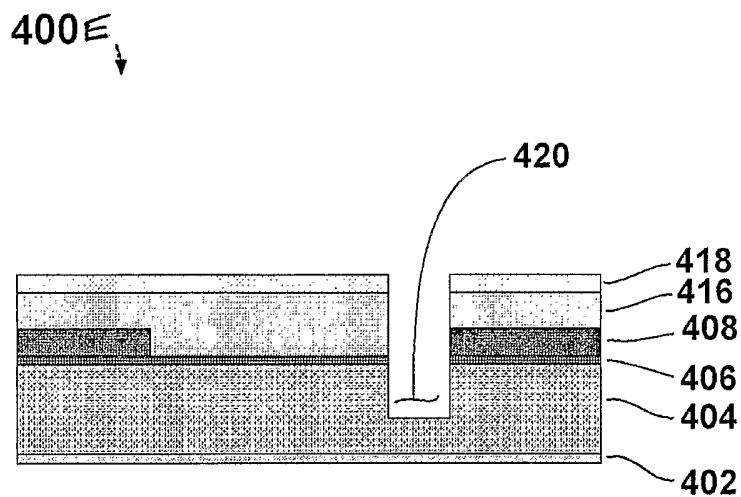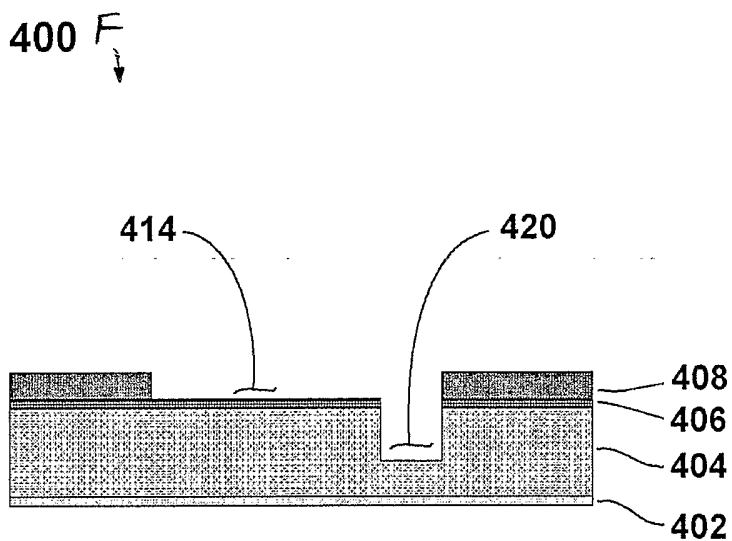
Figure 3F Prior Art.

400

Figure 3G Prior Art.

500 A

506
504
502

Figure 4A

500 B

510
508
506
504
502

Figure 4B

500C

512

510

508

506

504

502

Figure 4C

500D

514

506

504

502

512

Figure 4D

500E

518
516
506
504
502

512

Figure 4E

500F

520

518
516
506
504
502

512

Figure 4F

500G

520 — 514

— 504

— 502

512

Figure 4G

500 H

522 —

— 504

— 502

512

Figure 4H

600A

610

608

606

604

602

Figure 5A

600B

612

610

608

606

604

602

Figure 5B

600C

612

614

606

604

602

Figure 5C

600D

618

616

606

604

602

Figure 5D

600E

620

618
616
606
604
602

Figure 5E

600F

614

612   620

606

604

602

Figure 5F

Figure 5G