

ENHANCED FOCUSED ION BEAM ETCHING OF DIELECTRICS AND SILICON

Field of the Invention

[0001] This invention relates generally to focused ion beam (FIB) etching processes, and more particularly to focused ion beam gas assisted etching (GAE) of silicon and dielectrics based on silicon in integrated circuits (IC).

Background

[0002] Focused ion beam processes are widely used for debugging and verification of the functionality of integrated circuits (IC) and for IC circuit editing (CE) applications. Circuit editing involves the modification of individual IC circuits in order to correct design or manufacturing errors that cause IC malfunctions. FIB systems use a finely focused beam of gallium ions that can be operated in a wide range of beam currents from portions of pico-Amperes (pA) to tens of nano-Amperes (nA). Normally, the ion beam is scanned over an area of interest of a microchip producing emission of neutral or charged secondary particles. Neutral particles are mostly atoms and molecules sputtered from the scanned surfaces, and charged secondary particles are mostly secondary electrons and ions. Charged secondary particles are normally used in FIB instruments to form an image of the scanned area, so that its modification can be observed. The main purpose of FIB application for circuit editing (CE) is modification of the scanned area by either selective removal of specific materials (selective etching) or deposition of some specific materials, as, for example, having very low conductivity (insulators) or high conductivity (conductors). FIB systems provide for local "flooding" of a specimen with a variety of different gases. These gases can either interact with the primary gallium beam to provide selective gas assisted accelerated chemical etching or deposition of either conductive or insulating material by decomposition of the precursor gas by the primary ion beam.

[0003] As every IC structure comprises multiple layers of metal wiring interconnects and isolating materials (dielectrics), as well as bulk substrate semiconductor material, typically silicon (Si), CE modification typically involves some or all of four basic FIB processes. These are the selective etching of one or more dielectric layers to expose a

metal line or circuit of interest, the selective etching of metal to cut an interconnecting line of interest, the deposition of a metal conductor material to connect lines of interest, and the deposition of an insulator material to isolate lines or circuits. Since CE typically involves milling trenches or vias through layers of densely interleaved layers of metals and dielectrics to reach an area of interest, to avoid damage or destruction of the IC it is important that these FIB processes, particularly the etching of dielectrics and metals, be carefully controlled to selectively etch only the target material of interest and to minimize damage to other materials and structures of the IC. It is also important to avoid re-deposition of sputtered material removed by etching onto adjacent trench walls and surfaces of the IC.

[0004] An ion beam itself is a destructive agent causing only erosion or sputtering of the exposed solid material of the IC. It is possible to obtain desirable results such as selective etching and deposition of different materials by directing to the target surface where an FIB operation is being performed gaseous precursors for conductor or insulator deposition, or gaseous chemicals for selective gas assisted etching (GAE) of the target material. These chemicals are adsorbed on the surface, and the ion beam activates surface reactions resulting in either deposition or etching of the materials in the area exposed to the ion beam. To obtain a desired pressure of a gaseous agent in the spot of FIB operation, FIB systems use a small nozzle positioned very close to the target surface exposed to the ion beam. The chemical agents are directed to the target spot through this nozzle. In general, the result of any FIB operation depends on the chemistry used and the ratio between chemical pressure and ion dose delivered to the target spot of the operation. FIB systems enable adjustment of local pressure of the chemical agent and ion beam current so that the FIB process produces desirable results with good efficiency.

[0005] Currently, xenon difluoride, XeF_2 , is a widely used FIB dielectric etching agent for silicon dielectrics such as silicon dioxide, SiO_2 , and silicon nitride, Si_3N_4 . Almost all dielectrics used in IC manufacturing have silicon as one of their base elements. During FIB gas assisted dielectric etching using XeF_2 , silicon is oxidized by fluorine to form silicon fluoride, SiF_4 , which is a gas under normal conditions. This affords good efficiency and high selectivity when XeF_2 is used for etching dielectrics. Also, the gaseous by-products of the etching process are volatile and easily removed by the

vacuum pumping system so that the etched material by-products are not re-deposited on the walls of etched holes and other neighboring surfaces. Since in most cases, etching of a dielectric is used to expose a metal copper or aluminum line, an important advantage of using the fluorinating chemical XeF_2 for dielectric etching is that fluorine does not damage copper or aluminum. In contrast to other heavier halogens such as chlorine, bromine and iodine, fluorine does not corrode aluminum and copper deeper than few surface monolayers, which allows opening these materials with minimal damage. The heavier halogens create aluminum compounds that have spongy structure and can sublime with high vapor pressure at room temperature. Thus, traditionally they were used as very fast etchants for aluminum. However, these halogens (except fluorine) corrode copper material deeply which makes them inapplicable for exposing copper. Therefore, the only reasonable option for etching dielectrics in ICs to expose metal lines has been to use a fluorinating agent (rather than halogenating agent) as an etchant, and XeF_2 has been used as a dielectric etchant in FIB applications for years.

[0006] However, new developments in ICs technology have made XeF_2 inapplicable as an etchant in a number of applications. Because of the increasing complexity and density of active elements in ICs, a significant portion of modern ICs employ so called “flip-chip” packaging where access to the metal layers for CE must be obtained only through the transistor layer (or “active silicon”) of the microchip. This means it is necessary to expose the active silicon to FIB chemistries during CE work. Additionally, new “organic” or low-k dielectrics are increasingly being used instead of traditional SiO_2 , and there is an increasing tendency to employ a variety of other new dielectrics. XeF_2 is undesirable and problematic for flip-chip technology and these new materials.

[0007] It is very well known that XeF_2 corrodes bare silicon, i.e., it spontaneously etches silicon without ion beam assistance. This creates significant difficulties in “back-side” CE operations on flip-chip packaged ICs where active (bare) silicon is exposed, which is inevitable when doing “back-side” circuit edit operations. Fig. 1 illustrates the corrosion and damage of active silicon adjacent to the open metallization in a flip chip packaged IC during FIB etching with XeF_2 to expose the metal lines. The vulnerability of bare silicon to XeF_2 corrosion requires the application of protective coatings to the silicon prior to XeF_2 application. This makes CE operations longer and more complex.

[0008] In the case of dense active circuit elements in an IC, where FIB operation has to be performed very close to active silicon, the protective coatings can protect silicon from the top only, but not against natural lateral over-etch. This is illustrated in Fig. 2, which is a diagrammatic transverse view illustrating FIB etching of access holes through a silicon dioxide (SiO_2) shallow trench isolation (STI) layer of an IC to gain access to metal lines 20, 21. As shown, to gain access to line 20, the FIB access hole 28 must penetrate an FIB deposited protective dielectric 32 and pass through the SiO_2 layer 30 closely adjacent to silicon 34. This exposes the adjacent silicon area to lateral over-etch, by XeF_2 as shown at 38. The protective dielectric 32 deposited over the silicon areas may protect the silicon against XeF_2 corrosion from the top, but it does not protect it from lateral over-etching at the vertical (in the figure) sidewalls of the access hole.

[0009] Furthermore, it has been reported that some types of the new organic dielectrics show signs of corrosion under exposure to XeF_2 similar to those observed on silicon. This means that use of XeF_2 as a dielectric etchant is problematic not only for back-side CE applications, but also for front-side applications.

[0010] It is desirable to afford FIB process etch-assisting chemical compounds that address the foregoing and other problems of known dielectric etchants, that are non-corrosive to metals used for interconnects in ICs and have other desirable properties, and which will react with a solid specimen to produce volatile by-products that can be removed easily from the FIB vacuum chamber so that they are not re-deposited upon the specimen or neighboring surfaces. It is to these ends that the present invention is directed.

Summary of the Invention

[0011] In accordance with the invention, a FIB etching process is provided for silicon and IC dielectrics, including those containing silicon (Si), carbon (C), fluorine (F), oxygen (O), nitrogen (N) and even hydrogen (H), using chemistries that produce easily removed gaseous by-products, that afford close control over the etching process, and that avoid unwanted damage to bare silicon. Since fluorine, oxygen, nitrogen and hydrogen are gases, the FIB etchants of the invention produce volatile gaseous by-products with Si and C that are easily removed by the vacuum chamber pump to

provide clean etching of the target material of interest and do not re-deposit by-products on the neighboring surfaces.

[0012] In accordance with one aspect, the invention affords a method of etching and an organic fluorinating reagent triethylamine trihydrofluoride (TEATHF) as an etch assisting agent in a FIB process for etching silicon, silicon dielectrics, and low-k dielectrics.

[0013] In yet another aspect, the invention affords a method of etching silicon, silicon dielectrics and low-k dielectrics using xenon difluoride, XeF_2 , in combination with a secondary gaseous protecting agent that is chemically neutral (non-reactive) to XeF_2 and selected from the group of compounds consisting of oxygen, perfluorotripentylamine (PFTPA), and heavy completely fluorinated hydrocarbons and amines in a sufficient concentration to prevent corrosion of silicon.

Description of the Drawings

[0014] Fig. 1 is a microphotograph that illustrates the corrosion of bare active silicon adjacent to the open metallization in a flip chip packaged IC during FIB etching with XeF_2 to expose metal lines;

[0015] Fig. 2 is a diagrammatic view that illustrates the corrosion of active silicon closely adjacent to a trench etched by XeF_2 to access metal lines buried beneath an SiO_2 isolation layer between two areas of silicon;

[0016] Fig 3 is a microphotograph which shows an example of minimal or no damage to active silicon in an FIB etching process using XeF_2 in combination with a perfluorotripentylamine (PFTPA) protecting agent in accordance with the invention to open copper lines;

[0017] Fig. 4 is a microphotograph that illustrates the absence of damage to active silicon in a FIB etching process using TEATHF in accordance with the invention to open copper lines in an IC; and

[0018] Fig. 5 is a diagrammatic view that illustrates the mechanism of the invention in protecting silicon against corrosion by using a combination of XeF_2 and a protecting gaseous compound having a longer residence time than XeF_2 on the silicon surface.

Description of Preferred Embodiments

[0019] The invention is particularly well adapted to the gas assisted focused ion beam etching of silicon semiconductor materials and dielectrics for circuit editing of integrated circuits, and will be described in that context. It will be appreciated, however, that this is illustrative of only one utility of the invention and that the invention has greater applicability to other applications and to other types of materials.

[0020] Focused ion beam (FIB) systems that are useful for CE and gas assisted etching of dielectrics and semiconductor materials are well known and will not be described in detail herein. Examples of such FIB systems for gas assisted etching processes that may be used to practice the invention are shown in U.S. Patent Nos. 5,840,630 to Cecere et. al and 6,211,527 to Chandler, the disclosures of which are incorporated by reference herein.

[0021] Although conventional FIB apparatus and processes have typically employed Gallium (Ga^+) ions, different metal ions, non-metal ions, noble gas ions and molecular ions may also be used advantageously in FIB processes. For example, other metal ions that may be used include non-radioactive metal ions heavier than Gallium such as: Indium (In^+), Mercury (Hg^+), Silver (Ag^+), Gold (Au^+), Cesium (Cs^+), Barium (Ba^+), Yttrium (Y^+), Zirconium (Zr^+), Niobium (Nb^+), Molybdenum (Mo^+), Ruthenium (Ru^+), Rhodium (Rh^+), Palladium (Pd^+), Cadmium (Cd^+), Tin (Sn^+), Hafnium (Hf^+), Tantalum (Ta^+), Tungsten (W^+), Rhenium (Rh^+), Osmium (Os^+), Iridium (Ir^+), Platinum (Pt^+), Thallium (Th^+) and Lead (Pb^+). Non-metal mono-atomic ions that may be used include Germanium (Ge^+), Selenium (Se^+), Tellurium (Te^+) and Bismuth (Bi^+). Noble gas ions that may be used include Helium (He^+), Neon (Ne^+), Argon (Ar^+), Krypton (Kr^+) and Xenon (Xe^+), and molecular ions that may be used include $\text{NO}^{+/-}$, $\text{NO}_2^{+/-}$, $\text{N}_2\text{O}^{+/-}$, $\text{N}_2^{+/-}$, $\text{N}_2\text{O}_4^{+/-}$, $\text{CO}_2^{+/-}$, $\text{O}_2^{+/-}$, $\text{SiO}^{+/-}$, $\text{GeO}^{+/-}$, $\text{SiO}_2^{+/-}$ and $\text{GeO}_2^{+/-}$.

[0022] While the invention will be described herein using FIB process that employ Gallium ions, it will be appreciated that the invention is not dependent upon the particular ions used in the FIB process, and that other ions such as the ions mentioned above may also be used. From the description and examples that follow, one skilled in the art will be able readily to determine appropriate changes, if any, to the ion beam operating parameters that may be used for the selected ions.

[0023] As is well known, and as is shown in these referenced patents, an FIB instrument comprises a vacuum chamber with a holder for a specimen such as a microchip to be modified by the FIB process, an ion column, a gas delivery system (GDS) comprising a gas nozzle which can be positioned close to the microchip surface for delivering chemical etchants or precursors to a small localized target area on the microchip surface at adjustable pressure, and a system for scanning the ion beam over the microchip surface. Normally the nozzle to surface distance is between about 0.1 mm and 1 mm, and a navigation system allows precise positioning of the microchip with respect to the ion beam or vice versa. The specimen, e.g., the microchip which is to be processed, is installed in the vacuum chamber in such a way that it can be exposed to the ion beam, e.g., gallium ions, Ga^+ , at selected ion beam potentials of the order of 25 – 50kV out of the ion column, and also concurrently exposed to a chemical etchant/precursor gas stream from the gas nozzle of the GDS.

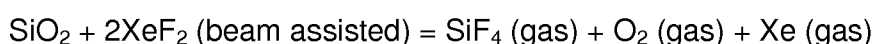
[0024] The ion beam current may be adjusted over a wide operating range, normally to a value within a range that is of the order of about 1 pico-Amperes (pA) or below to several tens of nano-Amperes (nA). The gas pressure in the localized area of interest is typically on the order of 0.05 – 1 torr, and is linearly correlated with pressure in the vacuum chamber with a coefficient of the order of $\sim 10^{-4}$. The base pressure in the chamber for no gas delivery is of the order of 10^{-7} to 10^{-6} torr, but when the gas is on, the pressure becomes about 0.5×10^{-5} to 10^{-4} torr. Pressures higher than about 6×10^{-5} torr are undesirable because this can result in damage to the ion column. Normally, the ion column has its own vacuum pumping system which affords external pressures of a maximum of about 10^{-4} torr. Otherwise, an automatic protection mechanism in the FIB system may close the column with a special gate.

[0025] FIB systems also incorporate an imaging system similar to that of a scanning electron microscope (SEM) for in situ process control. The imaging system may utilize secondary particle, e.g., secondary electron or secondary ion, emission caused by ion beam interaction with the exposed surface of the specimen to create an image of the target area.

[0026] During a FIB process, high energy ions that come into contact with the surface of the solid material of the specimen penetrate to deeper layers of the solid, creating cascades of atomic collisions. These collisions may produce many

generations of secondary recoils with decreasing energies as the number of the collisions increases. The higher the number of the collision, the more random the recoil motion direction is, with higher generations moving more isotropically. A significant part of these recoils returns to the surface of the solid causing sputtering and/or vibrational excitation of surface atoms. The excitation energy is on the order of a few electron-volts (eV), which is in the range of the activation energy of most chemical reactions. Therefore, if an absorbed chemical compound is present on the surface of the solid, an ion beam assisted chemical reaction can occur between atoms of the solid and the adsorbed chemical compound molecules of the gas.

[0027] Xenon difluoride, XeF_2 , is a fluorinating agent and an efficient etchant in a gas-assisted FIB process of silicon dielectrics, such as silicon dioxide, SiO_2 , and silicon nitride, Si_3N_4 , and of low-k dielectrics. As used herein, low-k dielectrics means dielectrics containing one or more of the elements silicon (Si), carbon (C), fluorine (F), oxygen (O), nitrogen (N) and hydrogen (H), and dielectrics containing fluorine doped silicon dioxide, carbon doped silicon dioxide, porous silicon dioxide, porous carbon doped silicon dioxide, silicone based polymeric dielectrics including hydrogen silsesquioxane (HSQ) and methylsilsesquioxane (MSQ), and polyimide. Low-k dielectrics containing such elements are readily etched by a fluorinating agent, such as XeF_2 , in the presence of an ion beam. XeF_2 also is an active etchant of silicon, Si. XeF_2 reacts with SiO_2 and Si in the presence of an ion beam as follows:



[0028] As shown, the by-products of the reactions are gaseous. Thus, they are easily removed by the vacuum system of the FIB, and re-deposition onto the solid specimen of etched material by-products is avoided. The presence in the specimen of carbon, or the other elements in the dielectrics described above which produce gaseous by-products, would not materially change the reaction. Carbon reacts with XeF_2 to create CF_4 which is also a gas, as are fluorine, nitrogen and hydrogen. Thus, carbon would behave as additional silicon in the specimen and would be volatilized in the same way.

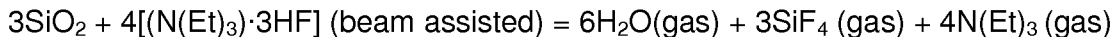
[0029] However, as described above, XeF_2 has the disadvantage that this compound reacts spontaneously with bare silicon without any assistance of an ion beam, and leads to aggressive and uncontrolled etching of the silicon. As a result, when using XeF_2 for CE on a microchip, very careful control is required to avoid exposure of so-called “active silicon” of the microchip, i.e., the silicon structures that form transistors and other functional elements of the device. If during the etching, some active silicon is exposed, it may be spontaneously corroded by XeF_2 causing damage to the microchip functionality, which is undesirable and may have negative consequences for the whole FIB circuit edit operation. This is illustrated in Fig. 1 which shows an example of damage to active silicon caused by XeF_2 in a conventional FIB etching process to open copper lines.

[0030] However, In accordance with the invention, it has been found that this disadvantage of XeF_2 may be overcome to avoid the corrosion of silicon by using XeF_2 in combination with one or more secondary protective agents that are non-reactive with XeF_2 and that protect Si, as will be described below.

[0031] In a preferred embodiment, the invention uses a newly discovered organic fluorinating reagent that has been found to be very effective and performs exceptionally well as an etchant in a gas assisted FIB processes for accelerating the etching of silicon and dielectrics, including silicon dielectrics and low-k dielectrics, but which does not spontaneously attack bare silicon. This organic fluorinating compound has desirable properties and avoids the problems with other known etchants, such as XeF_2 which corrodes silicon when used alone without a protecting agent, as will be described.

[0032] In accordance with the invention, the preferred compound which has been found that meets the above requirements is the organic fluorinating reagent triethylamine trihydrofluoride (TEATHF), which has the molecular formula $\text{N}(\text{Et})_3 \cdot 3\text{HF}$, where Et is the ethyl radical C_2H_5 . It has been experimentally confirmed that TEATHF, used alone without other agents, reacts to etch silicon and low-k dielectrics in a FIB process to produce gaseous products without damaging bare silicon. Fig. 4 illustrates the results of a FIB etching process using TEATHF to open copper lines in a silicon IC which uses SiO_2 as a dielectric. As shown in the figure, the metallization layer is nicely opened and exposed without damage to the active silicon. An equation of that

characterizes this reaction and shows that it produces volatile gaseous by-products is as follows:



[0033] The gaseous by-products of the process are easily handled, and are readily removed by pumping of the vacuum chamber, which avoids the deleterious effects of secondary re-deposition.

[0034] It has been found experimentally that TEATHF ((N(Et)₃) • 3HF) advantageously does not react spontaneously (without an ion beam) with bare Si, as does XeF₂, thus avoiding damage to the active silicon of an IC. Accordingly, TEATHF may be used as an etchant alone without other protective gases or agents. As a result, TEATHF affords good process control for dielectric etching without the danger of damaging the Si substrate of the specimen. TEATHF, while toxic, is stable, not exceptionally difficult to handle, and is readily available commercially. Working examples of using TEATHF as an etchant in a focuses ion beam process are given below in Table 2.

[0035] It should be noted that TEATHF is not a fluorinated hydrocarbon, which is the class of compounds disclosed by the referenced Chandler patent as etchants for a FIB process. The formula N(Et)₃ • 3HF of TEATHF means that three HF molecules are connected to the N(Et)₃ molecule by so-called hydrogen bonds which are electrostatic attraction bonds rather than chemical bonds. Both hydrofluoric acid (HF) and tributylamine (N(Et)₃) exist as individual chemicals. In contrast, fluorinated hydrocarbons are those where some or all hydrogen atoms are replaced with fluorine atoms, such as, for instance, trifluoroacetic acid, CF₃COOH (as compared to acetic acid, CH₃COOH) and trifluoroacetamide, CF₃CONH₂ (as compared to acetamide, CH₃CONH₂).

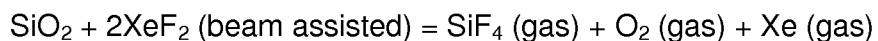
[0036] As described above, XeF₂ is a very powerful and well known fluorinating agent that has advantages as an FIB etchant, in spite of its ability to spontaneously attack bare silicon. Thus, XeF₂ is attractive as an etchant if corrosion of bare silicon can be avoided. In accordance with the invention, it has been found that this disadvantage of XeF₂ can be avoided by combining XeF₂ with one of several protective agents that have been found to protect bare silicon from spontaneous corrosion by

XeF₂. As will be described shortly, these protective agents comprise oxygen and certain heavy completely fluorinated hydrocarbons.

[0037] In accordance with an embodiment of the invention, oxygen may be used in combination with XeF₂ as a protective agent. Since silicon dioxide, SiO₂, is not vulnerable to spontaneous corrosion from XeF₂, by applying oxygen as a secondary gas along with XeF₂, the oxygen oxidizes Si to form a protective layer of SiO₂ over the silicon to avoid, thereby permitting control of the FIB etching process using XeF₂.

[0038] By applying ion beam irradiation to a target area of interest in bare silicon along with a flux of oxygen, the oxygen creates a thin layer of SiO₂ over the exposed silicon protecting it against corrosion during FIB etching using XeF₂. Importantly, oxygen does not react chemically with XeF₂. Therefore, the flux of oxygen may be delivered simultaneously with XeF₂ from either the same gas nozzle or from a separate gas supply nozzle in the FIB system, and the oxygen supply may be adjusted independently to afford a flux sufficient to protect against spontaneous corrosion during the etching operation.

[0039] As the material exposed to the ion beam in this case represents a mixture of Si and SiO₂, the chemical reaction of the etching process can be expressed as a combination of following equations:

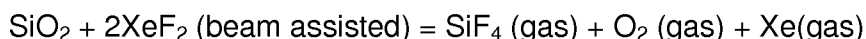


[0040] Outside of the etched area, the spontaneous corrosion is significantly inhibited by a thin layer of initially created SiO₂ as well as by reduced adsorption of XeF₂ in the presence of O₂ adsorption. Table 3, below, gives several working examples of process parameters that have been found to be effective and that afford good results.

[0041] In accordance with another embodiment of the invention, another protective compound that has been found to be effective in preventing corrosion of Si by XeF₂ when used as a secondary component with XeF₂ in FIB etching is perfluorotripentylamine (PFTPA), which has the molecular formula N[CF₃(CF₂)₄]₃. Importantly, PFTPA as a completely fluorinated compound does not react chemically

with XeF_2 . Therefore, the flux of PFTPA may be delivered simultaneously with XeF_2 from either the same or from a separate gas supply nozzle in the FIB system, and the PFTPA supply may be independently adjusted to a flux sufficient to protect against spontaneous corrosion during the etching operation.

[0042] When using a combination of XeF_2 and PFTPA for etching SiO_2 , one can neglect the reactivity of the PFTPA with SiO_2 as compared to the reactivity of XeF_2 . Therefore, the reaction in the area of the beam scanning will be substantially the same as if XeF_2 were present alone. The following equation characterizes the reaction of XeF_2 and SiO_2 :



[0043] There will be some decrease in the etching rate caused by the competing adsorption of PFTPA. But outside of the scanning area, PFTPA will significantly inhibit corrosion of the exposed silicon by the following described mechanism.

[0044] The dynamics of gas collection on the surface of a solid can be described by the following (simplified) formula:

$$C(t) = F \cdot \tau [1 - \exp(-t/\tau)],$$

where $C(t)$ is the amount of the gas present on the surface at an elapsed time, t , after the gas was turned on or all the gas was removed (desorbed) from the surface, for instance, by the ion beam, as explained below. F is the gas flux which is proportional to the gas pressure, and τ is the residence time of the gas molecules on the surface, i.e., the average time the molecules sit on the surface before evaporation. The population of the gas molecules on the surface is proportional to the product of gas flux and residence time. Thus, even at low pressure, the amount of a gas, i.e., the population of gas molecules, on the surface can be very high if the residence time is long enough.

[0045] Although PFTPA is volatile, it is a heavy compound, and its vapor pressure under normal conditions is about forty times (40X) lower than that of XeF_2 . This means that if both of the gases PFTPA and XeF_2 arrive at a surface with equal fluxes, after a long enough time the spot of gas incidence will be populated with PFTPA molecules about 40 times greater than with XeF_2 because of much longer residence time of PFTPA on the surface. Therefore, PFTPA will afford dynamic protection of the active silicon surface by blocking adsorption of XeF_2 .

[0046] Furthermore, even reducing the gas flux of PFTPA by, for example, eight times, will still leave PFTPA as the dominate adsorbent at about five times greater than XeF_2 . However, this occurs only where these adsorbents are competing with each other without interruption. In the spot of incidence where the scanning ion beam is etching silicon, the dynamics of the adsorbing processes will not be defined by the residence times of the adsorbents. Rather, the ion beam will be desorbing these adsorbents each time it completes a scan frame. If the scan frame time is shorter than the shortest residence time of the two gases, the ratio of gas populations at the scanned surface will be defined by the two gas fluxes, not by the gas residence times. Accordingly, if the gas flux ratio of XeF_2 to PFTPA is eight to one (8 : 1), then in the scanning area XeF_2 will dominate over PFTPA by a factor of eight times (8X), while outside of the scanning area PFTPA will be dominating, but by a factor of 5X because of the advantage of its greater residence time (40 : 1). The invention utilizes this advantage to protect active silicon outside of the scanned area from spontaneous corrosion by XeF_2 , as described below.

[0047] Fig. 5 shows curves of the differences in the amount of XeF_2 , a high vapor pressure, low residence time compound, collected on a surface as a function of time, and the amount of low pressure, long resident time protective agent PFTPA collected on the surface due to different in adsorption characteristics. As can be seen from the two curves for high pressure and low residence time XeF_2 and low pressure but very long residence time for PFTPA, if nothing disturbs the gases collected on the surface, then PFTPA dominates over XeF_2 at longer elapsed times. Thus, if the scanning ion beam has a frame rate selected such that it revisits each spot of the scanned area after a relatively short frame time as shown by the two arrows (approximately 20-30 milliseconds (mS) in the figure), then the ion beam sees a surface where XeF_2 dominates over PFTPA. Accordingly, gas assisted etching occurs substantially as if XeF_2 was present alone in the scanned spot. At the start of the next frame, the collection process is restarted. However, the large number of PFTPA molecules collected on the surface outside of the scan area is not desorbed by the ion beam and the molecules continue to build up, and must be applied at much lower pressure. With appropriate process parameters, the amounts of the compounds collection on silicon surface would go the way shown by the curves in the figure. Thus, by adjustment of the ion beam scanning time, the FIB process can ensure that the etching efficiency in

the area of the beam scanning would be sufficiently high to accomplish efficient etching in spite of the presence of the protecting gas, while protecting the areas of the silicon outside of the scanning area. Thus, the secondary protective gas is effective to protect the adjacent bare Si areas from spontaneous corrosion by XeF_2 . This method of adsorption control afforded by the invention advantageously and simply solves the problem of spontaneous etching of silicon to protect areas where the ion beam does not scan the surface.

[0048] PFTPA which is a preferable protective agent for use with XeF_2 is representative of a larger group of heavy chemicals which may be used in combination with XeF_2 to protect silicon from spontaneous corrosion. This group of compounds may be defined as:

1. Completely fluorinated hydrocarbons selected from the group of:
 - a) completely fluorinated alkanes having the general formula $\text{C}_n\text{F}_{2n+2}$;
 - b) completely fluorinated alkynes having the general formula $\text{C}_n\text{F}_{2n-2}$;
 - c) completely fluorinated alkenes having the general formula C_nF_{2n} ; and
 - d) combinations of the above, where the number of carbon atoms is greater than or equal to ten, i.e., $n \geq 10$; or
2. Completely fluorinated amines having the general formula NR_3 , where R is a radical and a derivative of the above completely fluorinated hydrocarbons with the formulas $\text{C}_n\text{F}_{2n+1}$, $\text{C}_n\text{F}_{2n-3}$, or $\text{C}_n\text{F}_{2n-1}$ or combination of these, and with $n \geq 4$.

[0049] As these compounds are completely fluorinated, they cannot be further fluorinated; thus they will not react with XeF_2 , which would inhibit or destroy its effectiveness as an etchant. The large numbers of elements in their fluorinated chains makes these compounds heavy and will provide high "stickiness" to surfaces which corresponds to long residence times.

[0050] In general, in a FIB process, efficiency, feasibility and productivity are defined by the ratio of the ion beam current density and etchant/precursor gas flux during a FIB gas assisted process. Current density by definition is the dose of ions delivered by the beam each second per square micron of the scanned area. Current density (in FIB practice) is normally measured in pico-Amperes per square micron ($\text{pA}/\mu\text{m}^2$). Gas flux is assumed to be proportional to the gas pressure in the working chamber during the

operation. Normally this pressure is adjusted to a preliminary recommended value by mass flow control valves or by controlling the temperature of the crucibles containing the compounds from which the gas is evaporated and delivered to the gas delivery system. All of the other parameters that can affect gas flux in the working spot, such as, for instance, gas nozzle positioning, may be standard values for conventional FIB processes. Accordingly, if the gas pressure is reasonably close to a recommended value, the only parameter that is important for the gas operation quality is the beam current density.

[0051] Preferred FIB process parameters for a FIB process in accordance with the invention which are applicable to the organic fluorinating reagent etchant TEATF as well as to the fluorinating etchant agent XeF_2 in combination with protecting gases such as oxygen and heavy completely fluorinated compounds as defined above may be as follows.

[0052] The gallium ions, Ga^+ , ion beam potentials are preferably adjusted to about 30 kV out of the ion column. The ion beam current is preferably adjusted to a value within the range of the order of about 1 pico-Amperes (pA) or below to several tens of nano-Amperes (nA) so that ion beam current density would be in the range of the preferred values for each etchant and/or combination of etchants as defined below. The preferred gas pressures and current densities are listed in the following Table 1, which gives specific preferred FIB process parameters for the etchants of the invention:

Table 1

Primary Chemistry	Secondary Chemistry	Preferred pressure of Primary Chemistry (torr)	Preferred pressure of Secondary Chemistry (torr)	Preferred Ion Beam Current Density for Dielectric Etching ($\text{pA}/\mu\text{m}^2$)
TEATHF	None	1.0×10^{-5}	N/A	3.0
XeF_2	PFTPA	3.0×10^{-5}	5.0×10^{-6}	5.0
XeF_2	O_2	3.0×10^{-5}	1.0×10^{-5}	5.0

[0053] The parameters in Table 1 are only for the invention. They are related to the preferred chemicals and combinations of chemicals described. The values of the preferred parameters in Table 1 may vary and assume values within the range of $\pm 30\%$ of the preferred values shown. Time is a parameter that will depend upon the thicknesses of the etched layers.

[0054] The following Tables 2-4 are, respectively, working examples for TEATHF, and for XeF_2 in combination with the secondary protecting agents oxygen and PFTPA. The Tables give different sets of parameter values that have been found useful and that produce good results for the different chemistries of the invention.

Table 2: Working Examples - TEATHF

Primary Etching Chemistry/ Pressure (torr)	Secondary Chemistry/ Pressure (torr)	Etched area size, (um x um)	Ion Beam Current, (pA)	Current Density (pA/um ²)	Etched Material/ Thickness (um)	Etching time min : sec
TEATHF /7.0E-6	None	2 x 1	5	2.5	SiO ₂ /1.0	3:25
TEATHF /6.7E-6	None	0.8 x 0.8	2	3.1	SiO ₂ /1.0	3:40
TEATHF /8.0E-6	None	1 x 1	3	3.0	Si/1.0	2:40

Table 3: Working Examples – XeF₂ and Oxygen (O₂)

Primary Etching Chemistry/ Pressure (torr)	Secondary Chemistry/ Pressure (torr)	Etched area size, (um x um)	Ion Beam Current, (pA)	Current Density (pA/um ²)	Etched Material/ Thickness (um)	Etching time min : sec
XeF ₂ / 2.5E-6	O ₂ /1.0E-5	2 x 1	10	5.0	SiO ₂ /1.0	1:49

XeF ₂ / 2.2E-6	O ₂ /1.1E-5	3 x 3	50	5.6	Si/5.0	12:46
XeF ₂ / 2.7E-6	O ₂ /1.0E-5	16 x 16	1056	4.13	Si/10.0	22:35

Table 4: Working Examples – XeF₂ and PFTP

Primary Etching Chemistry/ Pressure (torr)	Secondary Chemistry/ Pressure (torr)	Etched area size, (um x um)	Ion Beam Current, (pA)	Current Density (pA/um ²)	Etched Material/ Thickness (um)	Etching time min : sec
XeF ₂ / 2.4E-6	PFTP/ 5.0E-6	3 x 3	50	5.6	SiO ₂ /1.0	3:19
XeF ₂ / 2.6E-6	PFTP/ 4.3E-6	0.8 x 0.8	3	4.69	SiO ₂ /1.0	3:52
XeF ₂ / 2.6E-6	PFTP/ 4.8E-6	1 x 1	5	5.0	Si/1.0	3:40

While the foregoing has been with reference to certain preferred embodiments of the invention, it will be appreciated that changes may be made to these embodiments without departing from the principles and the spirit of the invention, the scope of which is defined by the appended claims.

CLAIMS:

1. A method of etching a specimen containing silicon and a dielectric, comprising placing the specimen in a vacuum chamber; directing a gas containing molecules of triethylamine trihydrofluoride (TEATHF) to a localized area of the specimen; and directing a focused ion beam to the localized area to etch material from the specimen.

2. The method of Claim 1, wherein said dielectric comprises a dielectric selected from the group consisting of silicon dioxide, silicon nitride, and low-k dielectrics containing elements selected from the group consisting of silicon, carbon, fluorine, oxygen, nitrogen, hydrogen and combinations thereof.

3. The method of Claim 1, wherein said dielectric comprises a low-k dielectric selected from the group consisting of fluorine doped silicon dioxide, carbon doped silicon dioxide, porous silicon dioxide, porous carbon doped silicon dioxide, polyimide, and silicone based polymeric dielectrics selected from the group consisting of hydrogen silsesquioxane (HSQ) and methylsilsesquioxane (MSQ).

4. The method of Claim 1, wherein said focused ion beam is scanned over said specimen at an average current density of between about $0.1 \text{ pA}/\mu\text{m}^2$ and several tens of $\text{pA}/\mu\text{m}^2$.

5. The method of Claim 4, wherein said focused ion beam is scanned over said specimen at an average current density of between about $1.0 \text{ pA}/\mu\text{m}^2$ and $8.0 \text{ pA}/\mu\text{m}^2$.

6. The method of Claim 5, wherein said ion current beam density is of the order of $2.5 \text{ pA}/\mu\text{m}^2$ to $3.0 \text{ pA}/\mu\text{m}^2$.

7. The method of Claim 1, wherein said TEATHF is supplied to provide a chamber pressure of between about 6.7×10^{-6} torr and 8.0×10^{-6} torr.

8. A method of etching a specimen containing silicon and a dielectric, comprising placing the specimen in a vacuum chamber; directing a gas containing molecules of xenon difluoride and a protective agent selected from the group consisting of oxygen and perfluorotripentylamine (PFTPA) to a localized area of the specimen;

and directing a focused ion beam to the localized area to etch material from the specimen.

9. The method of Claim 8, wherein said focused ion beam is scanned over said specimen at an average current density of between about $1.0 \text{ pA}/\mu\text{m}^2$ to $8.0 \text{ pA}/\mu\text{m}^2$.

10. The method of Claim 8, wherein said xenon difluoride is supplied to provide a chamber pressure of between about 1.0×10^{-5} torr and about 3.0×10^{-5} torr, and said protective agent is supplied to provide a chamber pressure of the order of 1.0×10^{-5} torr when said protective agent is oxygen, and supplied to provide a pressure of the order of about $4.0 - 5.0 \times 10^{-6}$ torr when said protective agent is PFTPA.

11. The method of Claim 8, wherein said protective agent is oxygen, and said oxygen is directed to said localized area with a sufficient flux to create a layer of silicon dioxide over bare silicon to protect the bare silicon from spontaneous etching by said xenon difluoride.

12. The method of Claim 8, wherein said protective agent is PFTPA, and said PFTPA is directed to said specimen with a sufficient flux to protect bare silicon from etching by said xenon difluoride.

13. The method of Claim 11, wherein a ratio of the flux of PFTPA to the flux of xenon difluoride is of the order of 1 to 8.

14. A method of etching a specimen containing silicon and a dielectric, comprising placing the specimen in a vacuum chamber; directing a gas containing molecules of a fluorinating agent to a localized area of the specimen, the fluorinating agent selected from the group consisting of triethylamine trihydrofluoride (TEATHF) and xenon difluoride in combination with a protective agent, the protective agent selected from the group consisting of oxygen, perfluorotripentylamine (PFTPA), and a completely fluorinated hydrocarbon; and directing a focused ion beam to the localized area to etch material from the specimen.

15. The method of Claim 14, wherein said protective agent is an agent that does not react chemically with xenon difluoride.

16. The method of Claim 14, wherein said protective agent is delivered to said specimen with a flux selected to protect silicon from spontaneous etching by xenon difluoride.

17. The method of Claim 14, wherein said protective agent is delivered to the specimen simultaneously with xenon difluoride.

18. The method of Claim 14 wherein said completely fluorinated hydrocarbon is a heavy compound that has a substantially lower vapor pressure than xenon difluoride.

19. The method of Claim 14, wherein said completely fluorinated hydrocarbon is selected from the group consisting of completely fluorinated alkanes having the general formula C_nF_{2n+2} , completely fluorinated alkynes having the general formula C_nF_{2n-2} , completely fluorinated alkenes having the general formula C_nF_{2n} , and combinations thereof, where the number, n , is greater than or equal to ten, and completely fluorinated amines having the general formula NR_3 , where R is a radical and a derivative of said completely fluorinated alkanes, alkynes, and alkenes with the formulas C_nF_{2n+1} , C_nF_{2n-3} , or C_nF_{2n-1} or combinations thereof, where the number, n , is greater than or equal to four.

20. The method of Claim 14, wherein said specimen is an integrated circuit, and said etching is performed for circuit editing.