

is etched. Typically, an ALE cycle includes a modification operation to form a reactive layer, followed by a removal operation to remove or etch only this modified layer. The cycle may include certain ancillary operations such as sweeping one of the reactants or byproducts. Generally, a cycle contains one instance of a unique sequence of operations. As an example, an ALE cycle may include the following operations: (i) delivery of a reactant gas, (ii) purging of the reactant gas from the chamber, (iii) delivery of a removal gas and an optional plasma, and (iv) purging of the chamber. In some embodiments, etching may be performed nonconformally. Figure 1B shows two example schematic illustrations of an ALE cycle. Diagrams 171a-171e show a generic ALE cycle. In 171a, the substrate is provided. In 171b, the surface of the substrate is modified. In 171c, the next step is prepared. In 171d, the modified layer is being etched. In 171e, the modified layer is removed. Similarly, diagrams 172a-172e show an example of an ALE cycle for etching a silicon film. In 172a, a silicon substrate is provided, which includes many silicon atoms. In 172b, reactant gas chlorine is introduced to the substrate which modifies the surface of the substrate. The schematic in 172b shows that some chlorine is adsorbed onto the surface of the substrate as an example. Although chlorine is depicted in Figure 1B, any chlorine-containing compound or suitable reactant may be used. In 172c, the reactant gas chlorine is purged from the chamber. In 172d, a removal gas argon is introduced with a directional plasma as indicated by the Ar^+ plasma species and arrows, and ion bombardment is performed to remove the modified surface of the substrate. During this operation, a bias is applied to the substrate to attract ions toward it. In 172e, the chamber is purged and the byproducts are removed.

[0029] A cycle may only partially etch about 0.1 nm to about 50 nm of material, or between about 0.1 nm and about 5 nm of material, or between about 0.2 nm and about 50 nm of material, or between about 0.2 nm and about 5 nm of material. The amount of material etched in a cycle may depend on the purpose of integrating with ALD. For example, if ALD is integrated to protect the sidewalls, then the amount etched in ALE cycles may be varied such that performing ALD protects the exposed sidewalls at the bottom of the feature. In some embodiments, a cycle of ALE may remove less than a monolayer of material.

[0030] Etching chemistry is introduced into the chamber in operation 103 of Figure 1A. As described herein, in operations where materials are introduced into the chamber, in some embodiments involving atomic layer etch using a plasma, the reactor or chamber may be stabilized by introducing the chemistry into the chamber prior to processing the substrate or wafer. Stabilizing the chamber may use the same flow rates, pressure, temperatures, and

[0038] ALD is a technique that deposits thin layers of material using sequential self-limiting reactions. ALD may be performed using any suitable technique. In various embodiments, ALD may be performed with plasma, or may be performed thermally. Operation 105 may be performed in cycles.

[0039] The concept of an “ALD cycle” is relevant to the discussion of various embodiments herein. Generally an ALD cycle is the minimum set of operations used to perform a surface deposition reaction one time. The result of one cycle is production of at least a partial silicon-containing film layer on a substrate surface. Typically, an ALD cycle includes operations to deliver and adsorb at least one reactant to the substrate surface, and then react the adsorbed reactant with one or more reactants to form the partial layer of film. The cycle may include certain ancillary operations such as sweeping one of the reactants or byproducts and/or treating the partial film as deposited. Generally, a cycle contains one instance of a unique sequence of operations. As an example, an ALD cycle may include the following operations: (i) delivery/adsorption of a silicon-containing precursor, (ii) purging of silicon-containing precursor from the chamber, (iii) delivery of a second reactant and a plasma, and (iv) purging of plasma from the chamber.

[0040] Figure 1B shows an example schematic illustration of an ALD cycle for depositing silicon oxide (SiO_2). Diagrams 182a-182e show a generic ALD cycle. In 182a, a silicon substrate is provided, which includes many silicon atoms. In 182b, oxygen is introduced to the substrate as oxygen radicals, which modify the surface of the substrate. This may be the delivery of the reactant and plasma. Note some oxygen radicals are adsorbed onto the surface of the substrate as an example. In 182c, the oxygen radicals are purged from the chamber. In 182d, a silicon-containing precursor or silicon source is introduced and the silicon source reacts with the oxygen radicals adsorbed on the surface of the substrate. In 182e, the chamber is purged and the byproducts are removed, leaving behind a deposited layer of SiO_2 .

[0041] In some embodiments, the films deposited by ALD may be highly conformal. Conformality of films may be measured by the step coverage. Step coverage may be calculated by comparing the average thickness of a deposited film on a bottom, sidewall, or top of a feature to the average thickness of a deposited film on a bottom, sidewall, or top of a feature. For example, step coverage may be calculated by dividing the average thickness of the deposited film on the sidewall by the average thickness of the deposited film at the top of the feature and multiplying it by 100 to obtain a percentage.

[0065] Methods described herein may be suitable for various applications. Examples of applications include: (1) high aspect ratio sidewall or mask protection, (2) MRAM (magnetoresistive random access memory) etching and encapsulation processes, and (3) selectivity improvement during directional etch processes.

[0066] In some semiconductor processes, soft materials, such as amorphous silicon or germanium, are directionally etched to form trenches or holes, or substrates with layers having such features in it may be exposed to directional etching. However, some neutral species may form in the trench or feature which may etch sidewalls of the features. An ALE process in small features in particular may cause sidewalls to be susceptible to lateral etching that may elongate the features. Methods described herein by integrating ALE and ALD processes, the film deposited during ALD may protect the sidewalls of these features from being etched during ALE. Likewise, these ALE and ALD integrated processes may be used to reduce corner faceting in masks, improve rigidity of a mask, and prevent degradation of a mask.

[0067] Conventional MRAM etching and encapsulation processes often involve exposing a moisture-sensitive layer, thereby risking contamination of the device. Although encapsulation is used in MRAM fabrication, encapsulation as described herein may also be used for other device fabrication and may be used for other sensitive layers.

[0068] In MRAM etching, an MRAM stack may include a tantalum mask deposited on an MTJ (magnetic tunnel junction), which is further deposited on a cobalt and/or tantalum layer, and a substrate. In some embodiments, there are more layers deposited between these layers. An MTJ may include two cobalt iron boron (CoFeB) layers, with a magnesium oxide (MgO) layer sandwiched between the two CoFeB layers.

[0069] This stack may be etched by first etching the ruthenium layer. In some embodiments, the tantalum layer may be etched by ALE. Subsequently, an argon or helium plasma may be used to etch and open the MTJ, thereby exposing a moisture-sensitive layer. Methods described herein allow the substrate to remain in the same chamber while ALD is then performed to deposit a thin encapsulation film over the moisture-sensitive layer and encapsulate it. In some embodiments, this thin encapsulation film is an oxide or nitride layer. In various embodiments, the cobalt and/or tantalum layer below may then be etched to break through to the substrate to continue etching the layer below.

[0070] Methods described herein may also be suitable for improving selectivity in etch

provided. The chuck 217 can be electrically charged using an RF power supply 223. The RF power supply 223 is connected to matching circuitry 221 through a connection 227. The matching circuitry 221 is connected to the chuck 217 through a connection 225. In this manner, the RF power supply 223 is connected to the chuck 217.

[0073] Elements for plasma generation include a coil 233 is positioned above window 211. In some embodiments, a coil is not used in disclosed embodiments. The coil 233 is fabricated from an electrically conductive material and includes at least one complete turn. The example of a coil 233 shown in Figure 2 includes three turns. The cross-sections of coil 233 are shown with symbols, and coils having an “X” extend rotationally into the page, while coils having a “●” extend rotationally out of the page. Elements for plasma generation also include an RF power supply 241 configured to supply RF power to the coil 233. In general, the RF power supply 241 is connected to matching circuitry 239 through a connection 245. The matching circuitry 239 is connected to the coil 233 through a connection 243. In this manner, the RF power supply 241 is connected to the coil 233. An optional Faraday shield 249 is positioned between the coil 233 and the window 211. The Faraday shield 249 is maintained in a spaced apart relationship relative to the coil 233. The Faraday shield 249 is disposed immediately above the window 211. The coil 233, the Faraday shield 249, and the window 211 are each configured to be substantially parallel to one another. The Faraday shield may prevent metal or other species from depositing on the dielectric window of the plasma chamber.

[0074] Process gases (e.g. chlorine, argon, silicon tetrachloride, oxygen, nitrogen, etc.) may be flowed into the processing chamber through one or more main gas flow inlets 260 positioned in the upper chamber and/or through one or more side gas flow inlets 270. Likewise, though not explicitly shown, similar gas flow inlets may be used to supply process gases to a capacitively coupled plasma processing chamber. A vacuum pump, e.g., a one or two stage mechanical dry pump and/or turbomolecular pump 240, may be used to draw process gases out of the process chamber 201 and to maintain a pressure within the process chamber 201. For example, the pump may be used to evacuate the chamber 201 during a purge operation of ALD. A valve-controlled conduit may be used to fluidically connect the vacuum pump to the processing chamber so as to selectively control application of the vacuum environment provided by the vacuum pump. This may be done employing a closed-loop-controlled flow restriction device, such as a throttle valve (not shown) or a pendulum valve (not shown), during operational plasma processing. Likewise, a vacuum

pump and valve controlled fluidic connection to the capacitively coupled plasma processing chamber may also be employed.

[0075] During operation of the apparatus, one or more process gases may be supplied through the gas flow inlets 260 and/or 270. In certain embodiments, process gas may be supplied only through the main gas flow inlet 260, or only through the side gas flow inlet 270. In some cases, the gas flow inlets shown in the figure may be replaced more complex gas flow inlets, one or more showerheads, for example. The Faraday shield 249 and/or optional grid 250 may include internal channels and holes that allow delivery of process gases to the chamber. Either or both of Faraday shield 249 and optional grid 250 may serve as a showerhead for delivery of process gases. In some embodiments, a liquid vaporization and delivery system may be situated upstream of the chamber 201, such that once a liquid reactant or precursor is vaporized, the vaporized reactant or precursor is introduced into the chamber via a gas flow inlet 260 and/or 270. Example liquid precursors include SiCl_4 and silicon amides.

[0076] Radio frequency power is supplied from the RF power supply 241 to the coil 233 to cause an RF current to flow through the coil 233. The RF current flowing through the coil 233 generates an electromagnetic field about the coil 233. The electromagnetic field generates an inductive current within the upper sub-chamber 202. The physical and chemical interactions of various generated ions and radicals with the wafer 219 selectively etch features of and deposit layers on the wafer.

[0077] If the plasma grid is used such that there is both an upper sub-chamber 202 and a lower sub-chamber 203, the inductive current acts on the gas present in the upper sub-chamber 202 to generate an electron-ion plasma in the upper sub-chamber 202. The optional internal plasma grid 250 limits the amount of hot electrons in the lower sub-chamber 203. In some embodiments, the apparatus is designed and operated such that the plasma present in the lower sub-chamber 203 is an ion-ion plasma.

[0078] Both the upper electron-ion plasma and the lower ion-ion plasma may contain positive and negative ions, though the ion-ion plasma will have a greater ratio of negative ions to positive ions. Volatile etching and/or deposition byproducts may be removed from the lower-sub-chamber 203 through port 222. The chuck 217 disclosed herein may operate at elevated temperatures ranging between about 10°C and about 250 °C. The temperature will depend on the process operation and specific recipe.