alkylphosphine, a phosphorus halide, an arsenic halide, a gallium halide, a boron halide, an alkylborane, or diborane.

In another aspect, a disclosed method deposits a dielectric film on a substrate surface in a reaction chamber. This method may be characterized by the following operations: (a) flowing an oxidant into the reaction chamber under conditions allowing the first reactant to adsorb onto the substrate surface; (b) introducing a dielectric precursor into the reaction chamber while the oxidant continues to flow into the reaction chamber; (c) exposing the substrate surface to plasma to drive a reaction between the dielectric precursor and oxidant on the substrate surface to form a portion of the dielectric film; (d) introducing a dopant containing material, not introduced during (a)-(c), into the reaction chamber under conditions allowing the dopant containing material to contact an exposed surface of the film; and (e) causing a dopant from the dopant containing material to integrate into the dielectric film. In one implementation, the dielectric precursor is BTBAS or another precursor as identified in the prior aspect.

Further, the method may require that operations (a)-(c) be repeated one or more times. In a specific example, the oxidant contains a first ratio of oxygen to nitrogen when (a) is initially performed but the oxidant contains a second ratio of oxygen to nitrogen when (a) is subsequently performed. The second ratio is smaller than the first ratio. For example, the oxidant may contain elemental oxygen when (a) is initially performed but contain nitrous oxide when (a) is repeated. In some embodiments, the substrate is at a first temperature when (c) is initially performed, and the substrate is at a second temperature, which is higher than the first temperature, when (c) is repeated.

In some cases, the method further includes driving the dopant from the dielectric film into the substrate. In some embodiments, the method further includes contacting the substrate surface with the dopant containing material prior to (a).

In another aspect, a disclosed method deposits a dielectric film on a substrate surface in a reaction chamber according to the following operations: (a) introducing a dielectric precursor into the reaction chamber under conditions allowing the precursor to adsorb onto the substrate surface; (b) thereafter purging the dielectric precursor from the reaction chamber while the precursor remains adsorbed on the substrate surface; (c) exposing the substrate surface to plasma to drive a reaction of the dielectric precursor on the substrate surface to form a portion of the dielectric film; and (d) introducing a dopant precursor, not introduced during (a)-(c), into the reaction chamber under conditions allowing the dopant precursor to contact the

a cycle may include the following operations: (i) delivery/adsorption of reactant A, (ii) delivery/adsorption of reactant B, (iii) sweep B out of the reaction chamber, and (iv) apply plasma to drive a surface reaction of A and B to form the partial film layer on the surface.

The seven above-mentioned features will now be discussed further. In the following descriptions, consider a CFD reaction in which one or more reactants adsorb to the substrate surface and then react to form a film on the surface by interaction with plasma.

*Feature 1* (Continuous flow of a reactant) – Reactant A continues to flow to a reaction chamber during one or more portions of a CFD cycle when the reactant would not normally flow in conventional ALD. In conventional ALD, reactant A flows only for the purpose of having the reactant adsorb onto the substrate surface. At other phases of an ALD cycle, reactant A does not flow. In accordance with certain CFD embodiments described herein, however, reactant A flows not only during phases associated with its adsorption but also during phases of a CFD cycle that perform operations other than adsorption of A. For example, in many embodiments, reactant A flows into the reactor while the apparatus is dosing a second reactant (reactant B herein). Thus, during at least a portion of a CFD cycle, reactants A and B coexist in the gas phase. Further, reactant A may flow while plasma is applied to drive a reaction at the substrate surface. Note that the continuously flowing reactant may be delivered to the reaction chamber in conjunction with a carrier gas– e.g., argon.

One advantage of the continuous flow embodiment is that the established flow avoids the delays and flow variations caused by transient initialization and stabilization of flow associated with turning the flow on and off.

As a specific example, an oxide film may be deposited by a conformal film deposition process using a principal reactant (sometimes referred to as a "solid component" precursor or, in this example, simply "reactant B"). Bis(tert-butylamino)silane (BTBAS) is one such principal reactant. In this example, the oxide deposition process involves delivery of an oxidant such as oxygen or nitrous oxide, which flows initially and continuously during delivery of the principal reactant in distinct exposure phases. The oxidant also continues to flow during distinct plasma exposure phases. See for example the sequence depicted in FIG. 1. For comparison, in a conventional ALD process, the flow of oxidant would stop when the solid component precursor is delivered to the reactor. For example, the flow of reactant A would stop when reactant B is delivered.

of these. These nodes are described in the International Technology Roadmap for Semiconductors (ITRS), the industry consensus on microelectronic technology requirements for many years. Generally they reference one-half pitch of a memory cell. In a specific example, the CFD processing is applied to "2X" devices (having device features in the realm of 20-29 nm) and beyond.

While most examples of CFD films presented herein concern silicon based microelectronic devices, the films may also find application in other areas. Microelectronics or optoelectronics using non-silicon semiconductors such as GaAs and other III-V semiconductors, as well as II-VI materials such as HgCdTe may profit from using the CFD processes disclosed herein. Applications for conformal dielectric films in the solar energy field, such as photovoltaic devices, in the electrochromics field, and other fields are possible.

FIG. 1 schematically shows a timing diagram 100 for an example embodiment of a plasma-activated CFD process. Two full CFD cycles are depicted. As shown, each includes an exposure to reactant A phase 120A or 120B, directly followed by an exposure to reactant B phase 140A or 140B, a sweep of reactant B phase 160A or 160B, and finally a plasma activation phase 180A or 180B. Plasma energy provided during plasma activation phases 180A and 180B activates a reaction between surface adsorbed reactant species A and B. In the depicted embodiments, no sweep phase is performed after one reactant (reactant A) is delivered. In fact, this reactant flows continuously during the film deposition process. Thus, plasma is ignited while reactant A is in the gas phase. Features 1-3 above are embodied in the example of FIG. 1.

In the depicted embodiment, reactant gases A and B may co-exist in the gas phase without reacting. Accordingly, one or more of the process steps described in the ALD process may be shortened or eliminated in this example CFD process. For example, sweep steps after A Exposure Phases 120A and 120B may be eliminated.

The CFD process may be employed to deposit any of a number of different types of film. While most of the examples presented herein, concern dielectric materials, the disclosed CFD processes may be employed to form films of conductive and semiconductor materials as well. Nitrides and oxides are featured dielectric materials, but carbides, oxynitrides, carbon-doped oxides, borides, etc. may also be formed. Oxides include a wide range of materials including undoped silicate glass (USG), doped silicate glass. Examples of doped glasses included boron doped silicate glass (BSG), phosphorus doped silicate glass (PSG), and boron phosphorus doped silicate glass (BPSG).

as described above, may assist with pressure and/or temperature control of the process station, evaporation of a liquid precursor, more rapid delivery of the precursor and may prevent back-diffusion of process station gases. In the embodiment shown in FIG. 14, an inert gas is continually supplied to the process station throughout reactant B exposure phase 140A.

In some embodiments, plasma activation of deposition reactions may result in lower deposition temperatures than in thermally-activated reactions, potentially reducing consumption of the available thermal budget of an integrated process. For example, in some embodiments, a plasma activated CFD process may occur at room temperature.

While the CFD process embodiment depicted in FIG. 1 is plasma activated, it will be appreciated that other non-thermal energy sources may be used within the scope of the present disclosure. Non-limiting examples of non-thermal energy sources include, but are not limited to, ultraviolet lamps, downstream or remote plasma sources, inductively-coupled plasmas, and microwave surface wave plasmas.

Further, while many examples discussed herein include two reactants (A and B), it will be appreciated that any suitable number of reactants may be employed within the scope of the present disclosure. In some embodiments, a single reactant and an inert gas used to supply plasma energy for a surface decomposition reaction of the reactant may be used. Alternatively, as discussed above in the context of feature 7, some embodiments may use three or more reactants to deposit a film.

In some scenarios, surface adsorbed B species may exist as discontinuous islands on the substrate surface, making it difficult to achieve surface saturation of reactant B. Various surface conditions may delay nucleation and saturation of reactant B on the substrate surface. For example, ligands released on adsorption of reactants A and/or B may block some surface active sites, preventing further adsorption of reactant B. Accordingly, in some embodiments, continuous adlayers of reactant B may be provided by modulating a flow of and/or discretely pulsing reactant B into the process station during reactant B exposure phase 140A. This may provide extra time for surface adsorption and desorption processes while conserving reactant B compared to a constant flow scenario.

Additionally or alternatively, in some embodiments, one or more sweep phases may be included between consecutive exposures of reactant B. For example, the embodiment of FIG. 2 schematically shows an example CFD process timing diagram 200 for a deposition cycle 210. At reactant B exposure phase 240A, reactant

deposition process. For example, deposition phase 1106 may include one or more of a CFD process, a CVD process, a PECVD process, etc. While the embodiment of FIG. 11 shows a single etch phase 1104, it will be appreciated that a plurality of in-situ etch processes may be inserted at intervals among multiple deposition phases of any suitable type during a gap fill process.

FIGS. 12A-C depict example cross-sections of a non-planar substrate at various phases of an embodiment of the in-situ deposition and etch processes described above. FIG. 12A shows a cross-section of an example non-planar substrate 1200, including a gap 1202. Gap 1202 is covered with a thin film 1204. Thin film 1204 is nearly conformal with gap 1202, but thin film 1204 includes a re-entrant portion 1206 near the top of gap 1202.

In the embodiment depicted in FIG. 12B, re-entrant portion 1206 of thin film 1204 has been selectively removed and that an upper region 1204A of thin film 1204 is thinner than a lower region 1204B. Selective removal of the re-entrant portion and/or sidewall angle adjustment may be achieved by imposing mass transfer limitations and/or lifetime limitations on the active etch species. In some embodiments, selective etching at the top of gap 1202 may also adjust a sidewall angle of gap 1202, so that gap 1202 is wider at the top than at the bottom. This may further reduce bread loafing effects in subsequent deposition phases. In the embodiment shown in FIG. 12C, after a subsequent deposition phase, gap 1202 is nearly filled and exhibits no voids.

Another embodiment of an in-situ etch process is shown in FIG. 15, which depicts a through-silicon via (TSV) ~~2500~~ for a copper electrode. Some example TSVs have depths of approximately 105 microns and diameters of approximately 6 microns, giving an approximately 17.5:1 aspect ratio, and may have a thermal budget ceiling of approximately 200 degrees Celsius. As shown in the embodiment of FIG. 15, through-silicon via 2500 is covered by a dielectric isolation layer 2502 to electrically isolate a silicon substrate from a metal-filled via. Example dielectric isolation layer materials include, but are not limited to, silicon oxide, silicon nitride, a low-k dielectric material. In some embodiments, the example etch processes described above may be supplemented with physical sputtering of the re-entrant portion using a suitable sputter gas, such as argon.

Other example applications for CFD films include, but are not limited to conformal low-k films (e.g., k approximately 3.0 or lower in some non-limiting examples) for back-end-of-line interconnect isolation applications, conformal silicon nitride films for etch stop and spacer layer applications, conformal antireflective

CFD DOPING EXAMPLES

CFD Boron-doped silicate glass (BSG) films were prepared and achieved nearly 100% step coverage on complex three-dimensional gate architectures. Similar results are expected with phosphorus-doped silicate glass (PSG). Boron or phosphorus can be driven from such films into the lateral and vertical regions of the source and drain junctions during a subsequent anneal step that provides conformal/homogenous under diffusion of the dopant. Figure 20 shows a typical deposition block used to synthesize a CFD BSG/PSG film. The CFD oxide growth cycle includes (a) a saturating dose of the $SiO_2$ precursor (BTBAS), (b) an inert purge to flush out remnant precursor species, (c) an oxidative plasma step, and (d) an inert gas purge to remove reaction by-products. This mechanism ensures that the reaction is self-limiting and promotes the excellent conformality observed with these films. A boron or phosphorus exposure step is periodically inserted during the CFD oxide growth, followed by a pump and purge sequence, and an optional RF pinning/cure step (e.g., exposure to plasma) if needed. This deposition block is repeated as many times as required by the target BSG/PSG thickness. See Figure 20.

While the frequency of insertion of boron or phosphorus exposure modulates the dopant diffusion distance at a given temperature, the length of exposure controls the total dopant dose. These two powerful control parameters provide a versatile synthesis scheme to accurately tune the interface dopant concentration.

In experiments, CFD has demonstrated excellent growth characteristics in BSG films. The CFD BSG process used BTBAS as the silicon source, $N_2O$ plasma for oxidation and 5% diborane ($B_2H_6$) in argon for boron doping. A mixture of argon and $N_2O$ was used as the purging gas. A growth rate of ~1A/cycle was obtained consistent with results on undoped CFD oxide, showing that the inclusion of a boron exposure step did not affect the CFD growth adversely. 250A-thick CFD BSG films exhibited near-perfect conformality on different test structures as shown by SEM photographs. Step coverage for these films was calculated to be ~100% on dense and isolated structures (Figure 21). Step coverage is defined as the quotient of film thickness on the sidewall of a feature divided by film thickness on the top of the same feature. Table ~~3~~ 6 shows the different splits from an initial study to partition out the effects of boron exposure time, frequency of the boron insertion and growth temperature on the final average boron concentration in the film. 25X CFD Ox means that there are 25 CFD undoped oxide cycles per boron insertion stage. This sample was grown to 500 Angstroms approximately, so the whole sequence was repeated around 20 times (given a growth rate of 1A/cycle for th CFD oxide). SIMS

data for these splits, as presented in Figure 22, show that the average boron concentration can be tuned in a range of about 0.5 – 3.5wt% boron, which enables customized doping options.

Table ~~3~~ 6

| *Label* | *Deposition Conditions* |
|---|---|
| CFDS1 | 400 °C/25x CFD Ox + 5s $B_2H_6$ exposure |
| CFDS2 | 400 °C/25x CFD Ox + 2.5s $B_2H_6$ exposure |
| CFDS3 | 400 °C/50x CFD Ox + 5s $B_2H_6$ exposure |
| CFDS4 | 350 °C/25x CFD Ox + 5s $B_2H_6$ exposure |

APPARATUS

It will be appreciated that any suitable process station may be employed with one or more of the embodiments described above. For example, FIG. 13 schematically shows an embodiment of a CFD process station 1300. For simplicity, CFD process station 1300 is depicted as a standalone process station having a process chamber body 1302 for maintaining a low-pressure environment. However, it will be appreciated that a plurality of CFD process stations 1300 may be included in a common low-pressure process tool environment. While the embodiment depicted in FIG. 13 shows one process station, it will be appreciated that, in some embodiments, a plurality of process stations may be included in a processing tool. For example, FIG. 14 depicts an embodiment of a multi-station processing tool 2400. Further, it will be appreciated that, in some embodiments, one or more hardware parameters of CFD process station 1300, including those discussed in detail below, may be adjusted programmatically by one or more computer controllers.

CFD process station 1300 fluidly communicates with reactant delivery system 1301 for delivering process gases to a distribution showerhead 1306. Reactant delivery system 1301 includes a mixing vessel 1304 for blending and/or conditioning