LOW TEMPERATURE SILCORE DEPOSITION OF UNDOPED AND DOPED SILICON FILMS

Safarmatov Uchqun Sohibjon o'g'li
Assistant, Almalyk Branch of Tashkent State Technical University

Introduction

The use of ultra-shallow junctions and high-k gate dielectric materials has resulted in a demand for lower thermal budget processing by device manufacturers (1-3). This requires that low temperature processes must be found to replace longstanding higher temperature process steps and enable new applications for novel integration flows. In this paper, a low temperature amorphous silicon process based on Silcore® chemistry is described. Silcore is a proprietary ASM™ version of purified trisilane Si3H8, manufactured by Voltaix. This process has been demonstrated for low pressure chemical vapor deposition (LPCVD) undoped amorphous silicon films and phosphorous-doped amorphous silicon films in a vertical furnace. Deposition of undoped, phosphorous, arsenic, and boron-doped amorphous, polycrystalline, or epitaxially deposited Si or SiGe films has also been performed in a single-wafer reactor. Silcore offers the possibility of reaching higher deposition rates than silane at lower deposition temperatures. This feature makes silcore an attractive candidate for the semiconductor device industry from the standpoint of thermal budget and cost of ownership considerations. In this paper, we will describe the results of studies performed examining silcore-based chemistry to obtain amorphous, polycrystalline, and epitaxial films. These experiments are performed for two hardware configurations: a LPCVD vertical furnace and a single wafer reactor capable of epitaxial deposition. While the silcore chemistry is the same for the two configurations discussed, the deposition is occurring in two different regimes: a thermal/kinetic regime in the vertical furnace and a mass-flow limited regime in the single wafer reactor. Initial results for dependence of the deposition results on temperature, pressure, and doping are described. Further observations regarding film properties, such as uniformity and surface roughness will also be described.

Experimental

Experimental The deposition of silcore-based films on 300mm silicon substrates has been evaluated in two different hardware configurations. Both configurations use silcore (proprietary ASM version of specifically purified and packaged Si3H8) chemistry. The vertical furnace configuration uses an ASM™ manufactured A412 LPCVD hotwall reactor which employs a quartz holderboat. The deposition pressure for all experiments described is 200mT, unless otherwise stated. All gases are delivered to the reactor via multihole injectors and the boat is rotated during processing. The silcore is delivered to the reactor via vapor draw from a liquid

bubbler. The silcore is delivered to the reactor using N2 as a carrier gas. The phosphorous source gas used in the described doped film experiments is PH3 (1% in N2). Secondary ion mass spectroscopy (SIMS) was used for depth profiling to determine the doping level, four point probe was used to determine the sheet resistance of the films following an anneal, and atomic force microscopy (AFM) was used to determine the surface roughness of the resulting films. For the phosphorous-doped silcore films that receive a furnace anneal, the wafers are annealed to 800°C in an N2 environment with measures taken to prevent phosphorous out-diffusion during the boat push and recovery steps of the anneal processing. Films were grown in an Epsilon® reduced pressure (RP) CVD single wafer epitaxial deposition tool manufactured by ASM™. The Epsilon® is a horizontal flow, load-locked reactor, featuring a lamp heated silicon carbide coated graphite susceptor in a cold wall quartz tube. In contrast to the vertical furnace, the wafers are sitting on a fast rotating susceptor that allows operating/processing under mass flow controlled/limited growth conditions. Wafer rotation, together with an optimized gas velocity profile, allows for compensation of strong depletion effects, resulting in excellent within wafer uniformities at much higher growth rates compared to truly reaction rate limited processes. The process conditions / tuning approach for the vertical furnace batch reactor and the single wafer reactor are therefore complementary. The nature of the wafer surface, together with the pre-growth wafer surface treatment (e.g. HF-last, in-situ bake) determines if the deposited film grows epitaxial or polycrystalline/amorphous. On insulators and on dense interfacial oxide the growth is amorphous or polycrystalline, whereas on exposed single-crystalline silicon surface after proper surface treatment the growth can be epitaxial (aligned with the underlying substrate).

Results/Discussion

Deposition Properties Vertical Furnace Deposition: For undoped silcore films deposited in an LPCVD vertical furnace, deposition rates ranging from 0.4–9Å/min have been demonstrated within the 410-500°C temperature range for N2 diluted silcore with partial pressures ranging from 3.9-11.3mT. In this temperature regime, all films obtained were amorphous. The deposition rate versus partial pressure as a function of temperature can be seen in Figure 1. These low partial pressures are typical for operation in a low deposition rate regime. The deposition rate can be significantly increased when the partial pressure of silcore is increased; deposition rates up to 63 Å/min were observed at 500°C when the partial pressure was increased to 80 mT.

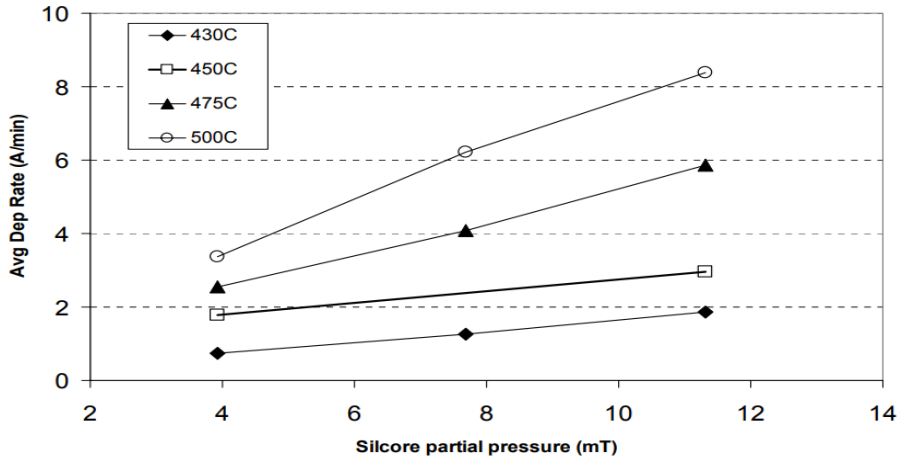


Figure 1. Silcore deposition (undoped) in the low deposition regime in a vertical furnace. The deposition rate [Å/min] versus silcore partial pressure [mT] are demonstrated as a function of deposition temperature [°C].

Phosphorous-doped silcore films have also been deposited on silicon substrates in the vertical furnace. Phosphorous-doped films with a doping level ranging from 3.8E19– 9.8E20atoms/cm3 have been deposited. The deposition rates observed for phosphorousdoped amorphous films are 0.4–4.6Å/min within the temperature range 410-490°C with silcore partial pressures ranging from 5.4-10.7mT. These results can be seen in Figure 2. These deposition rates are slightly lower than those observed for the undoped silcore films, especially at the higher temperatures. At the lower temperatures (≤ 450°C), minimal suppression of the deposition rate is observed. Figure 3 demonstrates the deposition rate as a function of increasing PH3 flow for two different vertical furnaces at 450°C; no suppression of the deposition rate is observed. However, as the deposition temperature increases to from 450 to 500°C, the deposition rate achieved is lower than that observed for the undoped films. This suppression of the deposition rate observed at higher temperatures is the opposite of that reported for phosphorous-doped silane films in vertical furnaces (4). The PH3 flow does not play a significant role in affecting the deposition rate, instead the PH3 flow determines the final phosphorous doping concentration in the film.

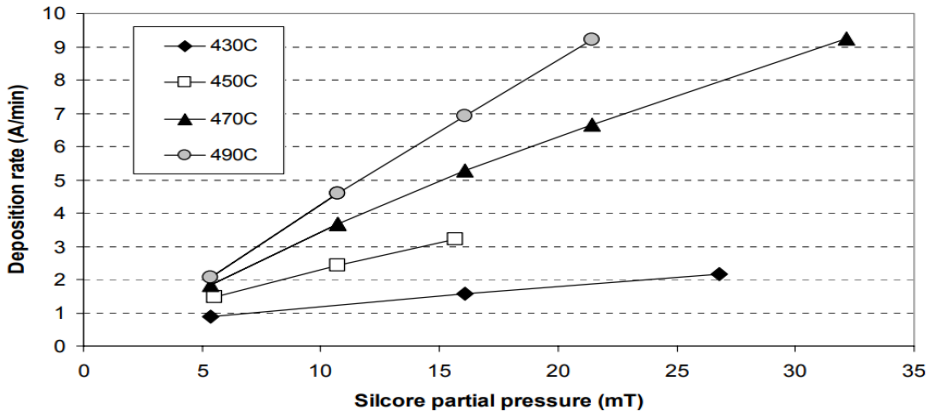


Figure 2. Phosphorous-doped silcore deposition in the low deposition regime in a vertical furnace. The deposition rate [Å/min] versus silcore partial pressure [mT] are demonstrated as a function of deposition temperature [°C].

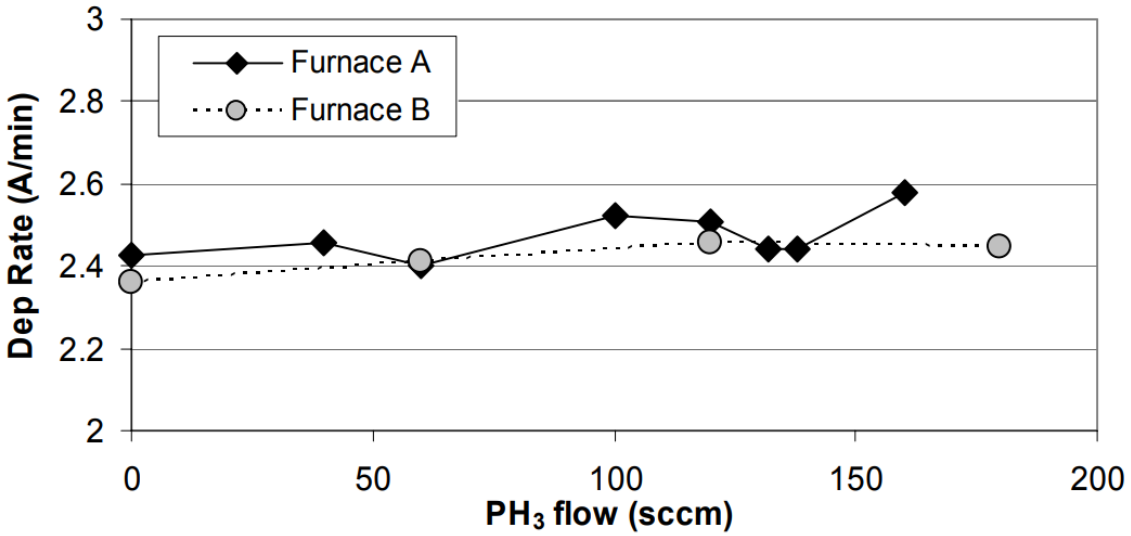


Figure 3. The deposition rate [Å/min] versus PH3 flow [sccm] at 450°C for two vertical furnace reactors. The deposition rate shows no indication of suppression as the PH3 flow is increased.

The observed deposition rate for pure silane (SiH4) films deposited in the same reactor is 3Å/min at 500°C and no deposition is observed for temperatures below 475°C. The deposition rate increases as temperature increases and rates of 12.5-30Å/min are observed from 520-550°C. For phosphorous-doped SiH4 films, typical deposition rates are 10–25Å/min for deposition temperatures in the range of 520-550°C. Some suppression of the deposition rate is observed when PH3 is used as a dopant for silane, typically becoming a smaller effect as the deposition temperature is increased (4). From this vertical furnace data, it is clear that silcore deposition can be achieved at temperatures significantly lower than those observed with silane, with comparable absolute deposition rates obtained. A direct comparison of silcore to silane is shown in Figure 4 with an Arrhenius plot comparing the amorphous films described.

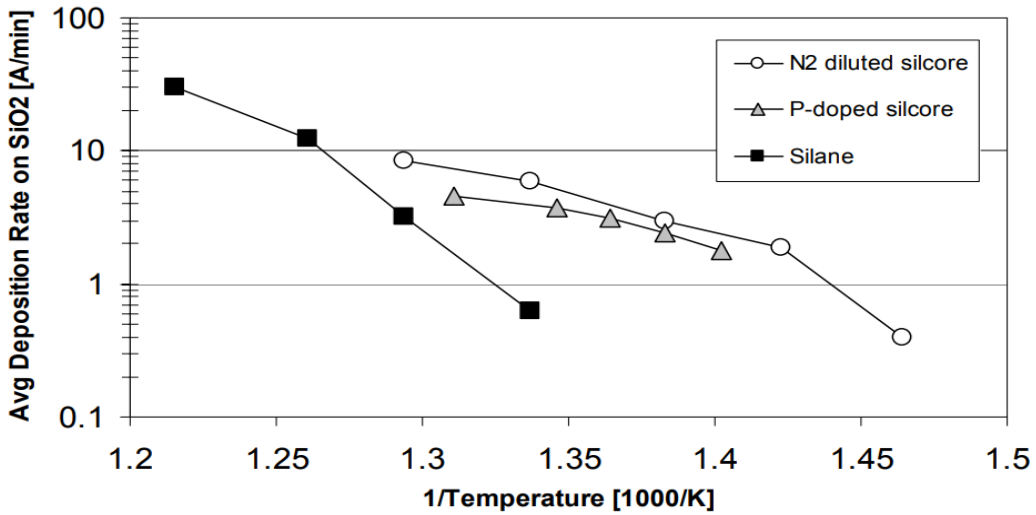


Figure 4. Arrhenius plot of silcore and silane deposition rate versus temperature for the vertical furnace configuration. The temperature range displayed is from 410 - 550°C.

Single Wafer Reactor Deposition: Silcore films deposited in the single wafer reactor can be amorphous or polycrystalline depending on substrate composition and deposition temperature. Amorphous and polycrystalline film deposition occurs over layers composed of SiO_2 or Si_3N_4. Epitaxial film deposition requires different substrate conditions, as will be discussed below. Film deposition in a vertical furnace is performed such that depletion effects are minimized (only the kinetic limited regime is useful). In contrast, a single wafer reactor with a rotating substrate allows for compensation of depletion if operated in the mass flow limited process regime, but it can still be operated under truly reaction rate limited conditions. Figure 5 shows a family of Arrhenius plots for different carrier gas flows and different total reactor pressures. Amorphous/poly growth rates were determined for a wide range of process conditions: temperature (400-1000°C), pressure (3-760 torr) and main carrier gas flow (5-100slm H_2). The Arrhenius plots show some very interesting features, in particular a distinct peak and a distinct valley. The thermal decomposition of silcore includes the elimination of SiH4. The low temperature region of the Arrhenius plot is related to deposition from the reactive intermediate Si2H4 or directly from Si3H8. The higher temperature region of the Arrhenius plot, left of the valley/minimum, can be related to deposition from the less reactive by-product SiH_4. Therefore the “net” Arrhenius plot can be considered as a superposition of two Arrhenius plots from different species (SiH4, Si2H4) with different reactivity (low, high), respectively. Depending on the silcore partial pressure (determined by the total reactor pressure, the main H_2 carrier flow, and the silcore mass flow) the transition between the mass flow and reaction rate limited regime varies by 200°C.

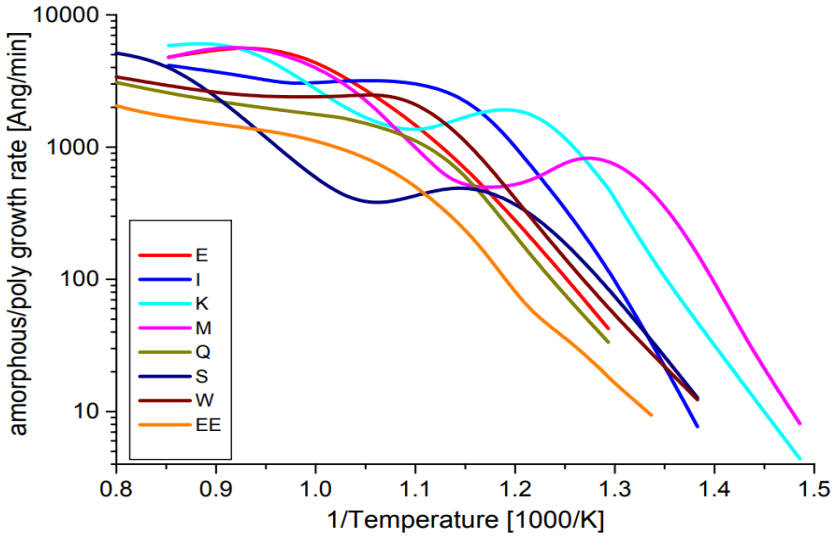
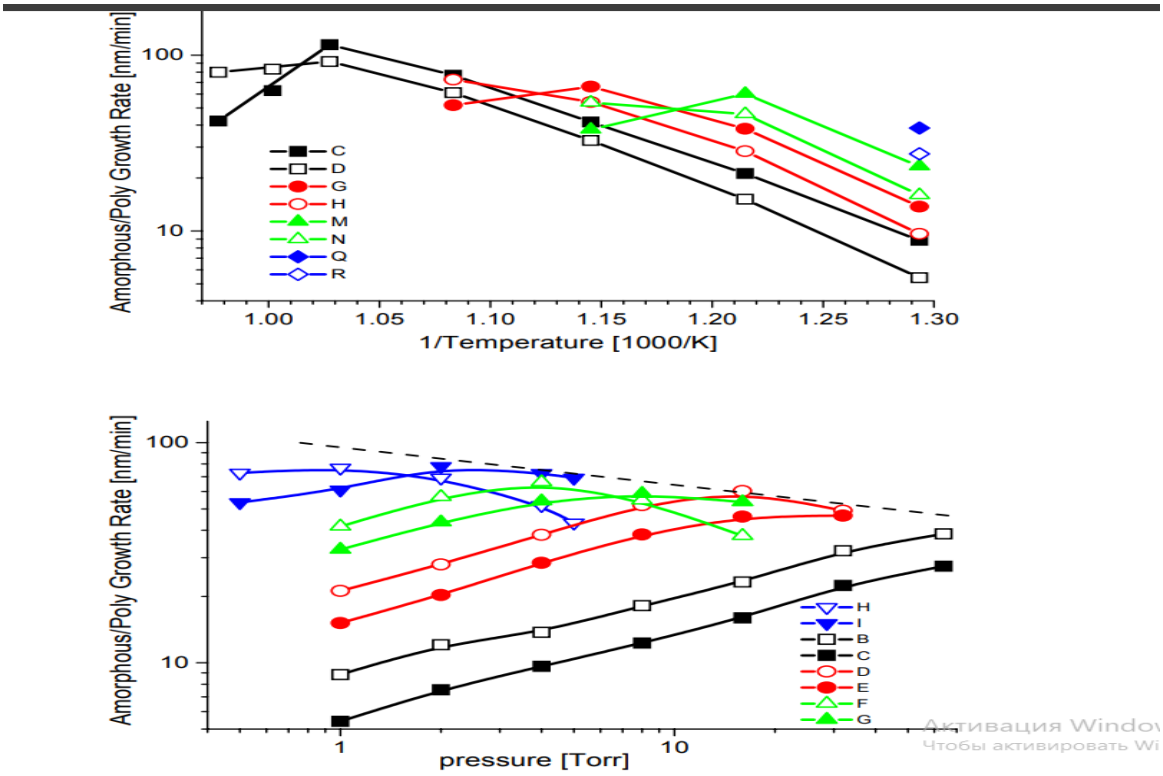


Figure 5. Arrhenius plot of silcore deposition rate versus temperature for various process conditions (H2 carrier gas flow [slm], pressure in [torr]). Distinct peaks and valleys (maximums and minimums) can be observed for some Arrhenius plots.

Figure 6a shows growth rate vs. reciprocal temp and figure 6b shows growth rate vs. pressure for amorphous/polycrystalline films deposited with a silcore mass flow of 50 mg/min and 2 slm H2 carrier gas flow. For low pressures (1 torr) the growth rate peaks around 700°C, while at a pressure of 16 torr the growth rate peaks around 550°C. For this set of experiments the edge of the wafer was purposely kept cooler than the center point, a depletion condition. This results in a non-uniform thickness profile where the center thickness less than the mean value of the within wafer thickness. The depletion condition can be compensated for by increasing reactor temperature, increasing total pressure, or decreasing carrier gas flow, so that the thickness at the center of the wafer becomes equal to the mean thickness value of the wafer, thus resulting in a uniform thickness profile. From Figure 6a, it can be seen that higher total pressure and lower carrier gas flow shifts that transition towards lower temperature, whereas lower pressures and higher carrier gas flows shift that transition toward higher temperature. In a single wafer tool the growth rate and silcore precursor utilization can be optimized/maximized for any particular temperature. Employing wafer rotation, an optimized gas velocity profile and/or purposely introduced temperature non-uniformity allows for (strong) depletion effects of the very reactive precursor to be compensated. Up to a certain limit, increasing the total pressure and reducing the carrier gas flow allows for the increase in growth rate and precursor utilization.



Figures 6. a, top) growth rate vs. reciprocal temp, and b, bottom) growth rate vs. pressure for amorphous/polycrystalline films deposited in a single wafer reactor with a silcore mass flow of 50 mg/min (growth rate [nm/min], temperature [K], pressure [torr]). In figure 6a, for low pressures (1 torr) and low carrier gas flow (2 slm H2) the growth rate peaks around 700°C, while at 16 torr the growth rate peaks around 550°C. Figure 7 demonstrates the growth rates of amorphous/poly Si deposition as function of silcore mass flow. The carrier gas flow was fixed at 5 slm H2, the pressure was chosen from figure 5 in order to get the maximum growth rate for a given temperature (500-550- 600-650°C). Growth rates of approximately 3 μm/min were achieved at 600-650°C at reduced pressure (32-16 torr) and up to 0.8 μm/min at 500°C and atmospheric pressure. For more complex films where dopant/resistivity uniformity, or SiGe, SiC alloy composition is critical, higher gas velocity (lower pressure, higher carrier gas flow) might be used in order to obtain excellent compositional uniformity.

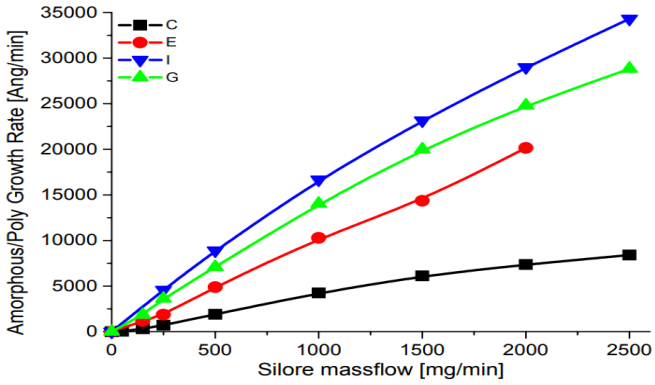


Figure 7: This figure shows growth rates of amorphous silicon deposition as function of silcore mass flow (temperature [°C], H2 flow [slm], pressure [torr]).

Epitaxial Deposition: Growth rates for epitaxial deposition depend on temperature, silcore partial pressure (total pressure, carrier gas flow, and silcore mass flow), and substrate preparation. Figure 8 shows epitaxial growth rates for phosphorous-doped silicon films as a function of total pressure, for a fixed temperature of 550°C. Deposition rates up to 100 nm/min were demonstrated with excellent film quality. Film resistivities as low as 0.35- 0.40 mΩcm were demonstrated for in-situ P and As-doped epitaxial films with electrical active dopant concentrations up to 6E20 atoms/cm3 . The impact of the dopant flow on growth rate is negligible. Figure 9 shows growth rates for epitaxial Si:C growth (for carbon doping levels of 1- 3 atomic %) as a function of temperature at a fixed pressure of 16 torr. The deposition rate is completely reaction rate limited under the process conditions chosen. The film uniformity, typically 1-2%, is determined by the thermal uniformity of the reactor.

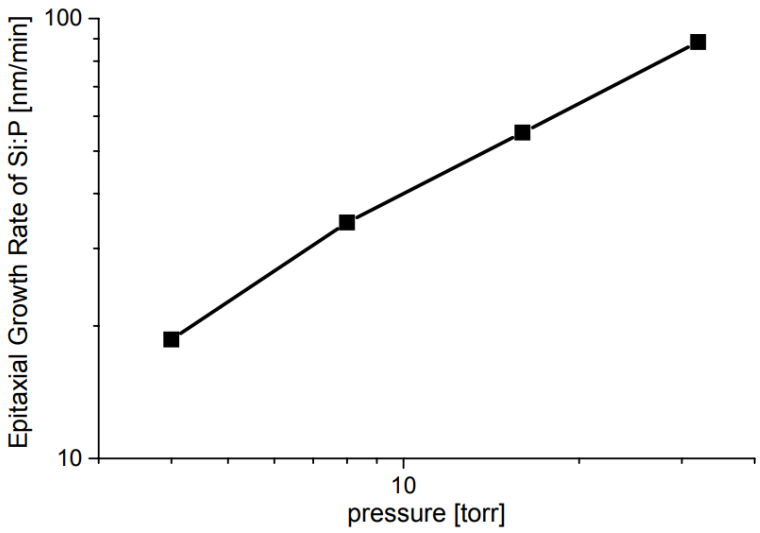


Figure 8. This figure shows the growth rate of epitaxial SiP [nm/min] as a function of pressure [torr] at 550°C.

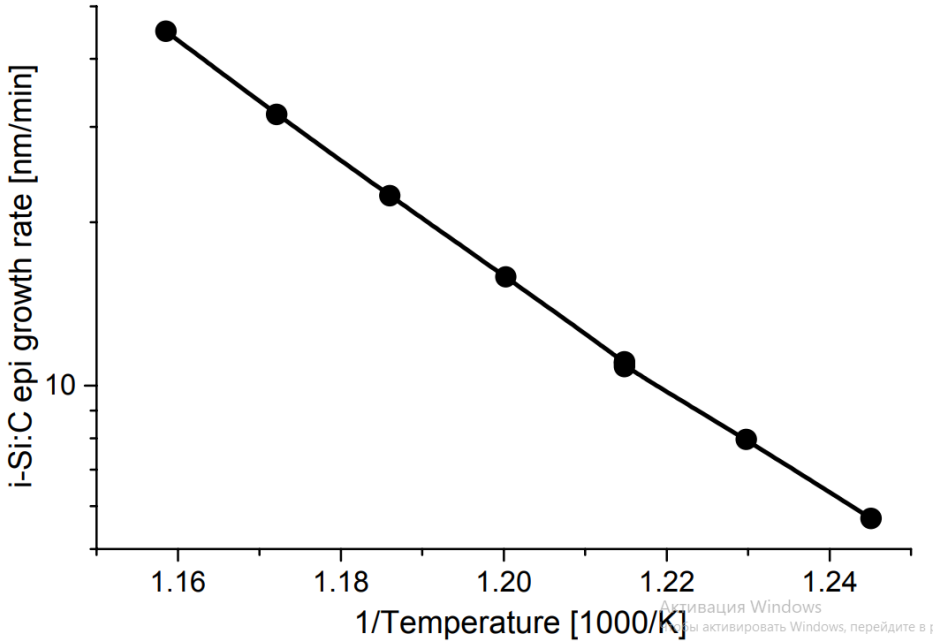


Figure 9. Arrhenius plot for the epitaxial growth rate [nm/min] of undoped Si:C as a function of 1/T [K] for the temperature range from 530-590°C at a reactor pressure of 16 torr.

Silcore Thermal Decomposition: The advantage of silcore chemistry is the lower deposition temperature regime available for the process. The silcore decomposition mechanism is non-trivial and directly impacts the resulting film properties. The thermal decomposition of silcore (in either the vertical furnace or single wafer reactor) is complex and multiple decomposition pathways have been proposed (5-11). Analytical modeling studies combined with FTIR analysis of the decomposition byproducts performed in our laboratories have identified two contributing reaction mechanisms. First, a direct reaction mechanism which results in the surface deposition of silicon on the wafer, is shown in equation [1]. Additionally, an indirect reaction mechanism occurs that includes a reactive gas phase intermediate as well as a surface reaction, equation [2a] and [2b], respectively.

$Si_3H_8 \rightarrow Si\ (s) + 2SiH_4$ [1]

$Si_3H_8 \rightarrow Si_2H_4\ * + SiH_4$ [2a]

$Si_2H_4\ * \rightarrow Si\ (s) + SiH_4$ [2b]

The observed deposition rate is a combination of the direct and indirect reaction rates as well as the component concentrations. The deposition rate data collected in the vertical furnace indicates that the indirect reaction (equations 2a, 2b) contributes approximately 25% to the overall deposition rate in the temperature regime from 410-500°C. The reaction mechanism presented here is also consistent with the results and

interpretation of the single wafer reactor data, specifically the observations from Figure 5. Fundamentally, silcore (trisilane) and silane are thermodynamically unstable (exothermic reaction); these species are stable due to an energetic barrier. However, the energy barrier can be crossed more easily by the silcore (Figure 4 demonstrates this experimental observation). This explains why silcore is reactive at lower temperatures than have been observed for silane.

Film Properties While the deposition rate of silcore films at lower temperature offers a processing advantage as compare to silane-based films, there are additional film properties that make silcore an attractive candidate for semiconductor devices. Silcore-based silicon films can be deposited with good within wafer uniformities, typically less than 1.5% for amorphous films deposited in vertical furnaces and less than 1% for films deposited in the single wafer reactor. Furthermore, the silcore-based amorphous films, both undoped and doped, show a significantly smoother surface as compared to silane-based films. This property of silcore films is appealing from a process integration perspective. For example, substrate pitting during the silicon etch process can be reduced due to the smooth nature of the silcore films as compared to silane films. Additionally, smooth silcore films may enable new applications for thin silicon films (potentially as hardmask layers or antireflective coatings) that are currently inaccessible to silane-based deposition methods. The silcore decomposition chemistry will also be discussed as the smoothness of the film is a direct result of the film nucleation and growth following decomposition. Film Uniformity: The indirect reaction, which includes the reactive gas phase intermediate Si2H4, is the primary contributor to non-uniformity in the vertical furnace. All furnace deposition data collected and an analytical study have shown that the indirect reaction mechanism is sensitive to the wafer pitch in the vertical furnace as well as the total exposed surface area available on which the reaction will occur. In a vertical furnace with a standard ASM quartz boat configuration, typical within wafer (WiW) 1σ uniformities observed are ~12-15% for films greater than 20nm in thickness. When additional surface area is provided at the edge of the wafer (the ASM “holderboat” configuration), the intermediate reaction can be “scavenged” thus improving the WiW uniformity to 1.5% WiW 1σ (4). Similar uniformities are observed for phosphorousdoped silcore films in a vertical furnace with thicknesses greater than 20nm. For comparison purposes, the WiW uniformities observed for pure SiH4 deposition in a vertical furnace utilizing a standard quartz boat configuration are silcore films (see Figure 11). In the single wafer reactor, epitaxially deposited films routinely achieve an RMS roughness of 2.8Å to 5Å.

Conclusions

This paper has described the deposition of silcore® in both a kinetic/thermal regime and a mass transfer limited regime for two hardware configurations, a vertical furnace and a single wafer reactor, respectively. The deposition properties and film

properties have been described. For both hardware configurations, undoped and doped silicon films can be deposited with.

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