Chapter 3

BASIC BPSG CVD KINETIC FEATURES

As we mentioned in Chapter 2, different chemistries (chemical compounds) can be used for BPSG thin film deposition. In this chapter, we briefly summarize basic SiO$_2$ and silicate glass film deposition kinetic features.

This is necessary for understanding the differences in thin film structure, composition and properties. Depending on the basic reaction chemistry used, silicon dioxide deposition kinetics (and silicate glass thin film) differed. The differences were found to be more pronounced for SiO$_2$ thin films, and they become less pronounced for silicate glass CVD kinetics.

The main difficulty with the adequate kinetic analysis was linked to a variety of the CVD reaction chambers that were used. To perform proper comparative analysis, it was necessary to use a valid methodology that could allow the definition of some commonalities and differences in CVD thin film kinetics.

In this Chapter 3, we briefly analyze the typical common thin film kinetic CVD features and summarize a methodology for thin film CVD kinetic analysis. The analysis combines a number of experimental data summarized previously for polysilicon, silicon nitride, silicon dioxide and glass thin film deposition. We then analyze basic silicon dioxide and silicate glass deposition features. This sequence will allow us to understand the data presented in Chapters 4 to 5.

3.1. BASIC THIN FILM CVD KINETIC FEATURES

In order to demonstrate the CVD kinetic basics regardless of the thin film nature, the following important CVD thin film features need to be highlighted for wafer samples with a flat surface [1-4,11,35-38,42-48].

(1) An analysis of thin film deposition kinetics is better if performed in dedicated tubular reaction chambers like hot-wall LPCVD, Figure 1.8(a), with relatively long and flat temperature distribution within the reactor, see Figure 1.8(b). This allows you to clearly see the basic features of thin film CVD kinetics - typical deposition rate (or kinetic) curves like presented in Figure 1.8(c) in general form. The shape of such curves typically revealed an increase, a maximum and a decrease area. The shape of
the curves and, especially, the position of the maximum on the curves, differ depending on the deposition chemistry and CVD process conditions. The analysis of maximum position gives the opportunity to establish its numerical characteristics for fast and simple CVD processes characterization.

(2) It is important to note that the squares under the kinetic curves, such as presented in Figure 1.8(c), are proportional generally to the deposited material quantities. According to the general chemical approach, the chemical synthesis should be performed at optimized reaction conditions, i.e. in the area close to the maximum, because the maximum position corresponds to the maximum of the CVD reaction yield. Therefore, the characterization of the thin film CVD process should be done after preliminary optimization of the reaction kinetics, i.e. after obtaining some kinetic curves and the determination of the maximum position on the curves. It is necessary to note that the determination of kinetic curves and their maximums is not an obvious procedure, especially because of the variety of CVD reactors used. We highlight the main methodology aspects for this procedure. General approaches about the theory and methodology of CVD reactions can be found in [1-4].

(3) The shape of the reaction curve and the position of the maximum on the curve with respect to the CVD reactor length always depend on the process variables (temperature, pressure, etc.). It is very important to highlight that at the constant CVD temperature and CVD pressure it also depends on the total gas flow \( G_0 \). The higher total flow value corresponds to the longer maximum position in the tubular reactor, as shown in Figure 1.8(c). This observation plays the crucial role in the understanding of CVD thin film kinetics.

(4) An analysis of silicon nitride experimental data in hot-wall tubular LPCVD reactors allows us to make a very important conclusion. After special re-calculation, typical kinetic curves presented in Figure 1.8(c) coincided with the so-called “time curve” (see Figure 1.9 [42]). This kinetic time curve was derived from experimental data. Instead of the wafer coordinate in the reactor, a so-called “residence time” \( \tau \) coordinate was used. The latter was calculated as follows: \( \tau = (x_i - x_0)/\nu \), where \( x_i \) is the substrate coordinate in the reactor (cm, mm), and \( \nu \) is the gas flow speed (or gas velocity), for instance, expressed in m/s or cm/s. Here the point \( x_0 \) corresponds to a coordinate of the beginning of the film growth in the reactor. This can be found only experimentally, analyzing the beginning of the film appearance on the quartz tubular reactor side walls. It is obvious that the gas flow speed is proportional to the total gas flow. Therefore, the curves presented in Figure 1.8(c) are the same in shape as the curves presented in Figure 1.9 (top right) because \( G_0(1) \sim \nu_1 \), \( G_0(2) \sim \nu_2 \), \( G_0(3) \sim \nu_3 \) (under the same other CVD conditions).

Gas flow speed values differ by a few orders of magnitude depending on the CVD process conditions. The largest \( \nu \) values, up to tens of meters per second, are typical for LPCVD systems. The smallest \( \nu \) values, like a few tens of cm/s, are typical for APCVD conditions. Using the examples of tubular APCVD and LPCVD reactors with cross-square \( s_R, [cm^2] \), and the gas flow speed can be easily calculated using formulas (1.4) and (1.5), accordingly:
Figure 1.8. Sketch of hot-wall tubular LPCVD with horizontal substrates placement (a), typical shape of deposition temperature distribution along with reactor length (b) and typical shapes of kinetic curves obtained at different process flows $G_0$ and some other CVD process conditions (c). Definitions are the same as in Figure 1.4.

\[
\nu_{APCVD} = \frac{G_0 \times T_d}{s_R \times T_r},
\]

(1.4)

\[
\nu_{LPCVD} = \frac{G_0 \times T_d \times P_d}{s_R \times T_r \times P_a},
\]

(1.5)

where $T_d$ and $T_r$ are the deposition and room temperature, K, accordingly, and $P_d$ and $P_a$ are the deposition and atmospheric pressure, torr, accordingly.

Figure 1.9. Kinetic time curve calculation example (see details in the text).
Thus, the time curve for a pre-selected set of CVD thin film process conditions can be obtained experimentally by changing only the total gas flow rates while keeping constant the other process conditions.

(5) The time curve analysis allows the definition of two basic kinetic parameters (see Figure 1.9): the absolute value of the deposition rate in maximum ($W_{\text{max}}$) and corresponding residence time value $\tau_{\text{max}}$. These two characteristics always change in shape and values depending on the process conditions, as shown in Figure 1.10 in general form. In this graph, one can see that an increase of deposition temperature and deposition pressure cause the increase of $W_{\text{max}}$ and its shift to the shorter $\tau_{\text{max}}$ value, and vice versa. This graph clearly shows that proper CVD thin film process analysis in any reactor should be performed taking into account real kinetic time curves. For instance, by placing the only one control substrate just at the same place in the tubular reactor that is indicated as A, B, C, D in the graph, a researcher will get the wrong kinetic trends, as detailed in the top right corner of the graph.

(6) According to classical chemistry, the coincidence of kinetic curves presented in Figure 1.8(c) into the time curve presented in Figure 1.9 and Figure 1.10 indicates that CVD process conditions in flow reactor used corresponded to the so-called “plug reactor” conditions. The main important feature of the plug reactor is that the residence time $\tau$ is equal to the chemical reaction time. Thus, the kinetic time curves in Figure 1.9 and Figure 1.10 represent the features of studied chemical reaction. This is a very important conclusion because it provides the basis for accurate proposals regarding the process schemes of CVD thin film reactions.

(7) The kinetic curves presented in Figure 1.9 and Figure 1.10 using the example of the tubular reactor can be in part obtained in any other flow-type CVD reactors. However, it is necessary to highlight that for single-wafer chambers with showerheads, the parameter $x_i$ is equal to the spacing between the showerhead and the wafer surface. In this case, the re-calculations give a good coincidence of the kinetic curves [224].

(8) The analysis presented above allows us to find the proper experimental methodology for CVD thin film process characterization. For instance, the right way to analyze CVD kinetics is to register the kinetic curves in order to find the values of $W_{\text{max}}$ and $\tau_{\text{max}}$. We accept that in many cases the experimental work cannot be done in a wide range of process parameters. Nevertheless, even one completed kinetic time curve that can be roughly calculated based on small volume experiments, can give the basic understanding of the studied CVD process and CVD tool conditions.

(9) The other CVD process characterization includes, for instance, a search for an order of CVD reaction with respect to the used compounds, an activation energy calculation, etc.

A simplified example of chemical reaction of two compounds (A and B) with formation of thin solid film (D) and a gaseous by-product (E) can be presented in general form as follows (1.6):

$$aA + bB \rightarrow dD + eE$$  

(1.6)
According to the classical chemistry, the rate of chemical reaction \( W \) can be written as follows (1.7):

\[
W = k_f \times [C_A]^a \times [C_B]^b,
\]

(1.7)

where, \( k_f \) – coefficient of proportionality, or reaction constant; \([C_A], [C_B]\) – concentrations of A and B compounds; \(a \) and \(b\) – stoichiometric coefficients, which are equal to the reaction orders with respect to compounds A and B. It was observed that the studied thin film CVD reactions revealed mostly the first order with respect to the silicon compounds used for CVD [1-3]. At the same time, CVD thin film reactions were conducted typically at considerable excess of the second compound (oxidizer or ammonia). This indicates the pseudo zero reaction order with respect to the second compounds that is shown in general form in Figure 1.11(a) as concentration dependencies \( W = f([C_i]) \). This conclusion was reached for all studied silicon-base thin film CVD thin film processes [1-3]. This conclusion allowed the simplification of the CVD thin film characterization. As for the activation energy, \( E_a \), its value is normally calculated using equation (1.8) and temperature dependence like presented in Figure 1.11(b):

\[
k_f = k_0 \times \exp\left(\frac{-E_a}{RT_d}\right),
\]

(1.8)

where \( k_0 \) is a coefficient of proportionality and \( R \) is a gaseous constant. For CVD thin film processes, \( E_a \) was variously reported to be \( 62 – 209 \text{ kJ/mol} \) except for PECVD, in which \( E_a \) is usually lower by an order of magnitude.

(10) Summarizing thin film CVD kinetic information, it was concluded that the film deposition rate \( W_{\text{max}} \) can be considered as the only important gas-phase deposition process parameter. In order to exclude any influence of the deposition process parameters, a generalized parameter named an “effective constant of the deposition rate, \( k_{\text{eff}} \)” [cm/s] was established in [1,2]. The lower \( k_{\text{eff}} \) value corresponds to the slower CVD process and vice versa.
The parameter $k_{eff}$ can be easily calculated based on the experimental kinetic curves using the deposition rate values in the maximum ($W_{max}$), and silicon compound concentration $[C_{Si}]$ as follows:

$$k_{eff} = \chi \frac{W_{max}}{[C_{Si}]}$$  \hspace{1cm} (1.9)

where $\chi$ is the coefficient of proportionality and $[C_{Si}]$ is calculated using the well-known equation (1.10) according to equation (1.11):

$$p_i \times V = n_i \times R \times T_d$$  \hspace{1cm} (1.10)

$$[C_{Si}] = \frac{n_{Si}}{V} = \frac{p_{Si}}{R \times T_d},$$  \hspace{1cm} (1.11)

where $p_{Si}$ is a partial pressure of silicon compound, $n_{Si}$ is a number of silicon compound moles. Below we show that $k_{eff}$ value is a main kinetic parameter that allows the description of the most of obtained CVD thin film experimental data.

In conclusion, it follows from the above discussion that basic measurable CVD process parameters ($T_d$, $P_d$, etc) are insufficient for proper CVD kinetic characterization. The analysis must include the residence time determination.

### 3.2. Basic Silicon Dioxide Thin Film CVD Kinetic Features

The kinetic analysis presented above is applicable for all types of CVD thin film processes. In this paragraph we briefly focus on the silicon dioxide thin film kinetic features. Based on accumulated experience, we would like to highlight two important features: basic reaction chemistry and the oxidation compounds used.

![Figure 1.11. Typical concentration dependencies (a) and reaction temperature dependence (b) (in general form).](image-url)
Figure 1.12. Typical silicon dioxide thin film kinetic curves obtained in tubular hot-wall CVD reactor with flat temperature profile, see Figure 1.8(a,b). Explanations are in the text.

(1) As we have already mentioned above, silane-based and TEOS-based chemistries have been used for silicon dioxide and silicate glass film deposition. These chemistries revealed totally different CVD kinetic peculiarities. The main difference can be illustrated by typical kinetic curves obtained in tubular hot-wall CVD reactors and presented in Figure 1.12 in general form. The curve 1 in Figure 1.12 is typical for relatively low deposition rate TEOS-based processes. The curve 3 is typical for high deposition rate silane-based processes. Severe differences in the shapes of these types of kinetic curves will be explained in detail in the next chapter by the difference in CVD reaction schemes and mechanisms. Another feature of silicon dioxide CVD processes is the capability of aerosol formation during the film deposition. It is necessary to emphasize that according to accumulated experimental data, silane-based chemistry is much more prone to form particles in the gas-phase of CVD reactors [3]. This is also explained by the difference in the reaction mechanism. It is important to highlight that aerosol formation effects were found to appear at enhanced CVD working temperatures and pressures, as well as at longer residence times. The latter can be explained by the appearance and development of side gas-phase reactions. These observations indicated that areas of the deposition rate decrease in kinetic curves presented in Figure 1.12 are significantly less applicable for the high-quality silicon dioxide thin film deposition. It is necessary to mention that this conclusion, in general, is applicable for the other types of CVD thin films, but silicon dioxide thin film CVD serves as the best example.

As for the curve 2, it is typical for CVD processes with acceleration effects. This process starts with a low deposition rate followed by sharp acceleration up to a high deposition rate. This curve was found by the author to be representative for two studied chemical systems: SiH₄-N₂O and DMDCS-O₂[1,2]. Both reactions were studied in a mid-temperature range in tubular hot-wall LPCVD apparatus.

(2) The type of second reaction component, i.e. oxidant, was found to be also very important for CVD. Historically, oxygen was considered to be the main oxidation agent. However, “soft” oxidizers like CO₂ and N₂O were also examined in the reaction with silane that was reviewed in [3,42]. It was found that their main disadvantage is the relatively low deposition rates as those provided by oxygen. As a
result, these two oxidizers could be used at a significantly higher CVD temperature (above ~ 600 °C) that is in contrast with many IC technology requirements. Another negative feature of these soft oxidizers is the impossibility to use these compounds to deposit silicate glasses during the thermal activation of the gas-phase. Phosphorus additives were found to suppress the CVD processes with N₂O as the oxidizer [1-3]. As a result, these oxidizers, preferably N₂O, were used for the only PECVD processes.

The last attempt to use a different oxidizer was done at the end of 1980 [96]. It was found that ozone can play a very important role in the reaction with TEOS, significantly enhancing the deposition rate of thermally-activated CVD processes at low temperatures. In Figure 1.13(a), some temperature dependences for TEOS-based silicon dioxide CVD are presented using data [304] obtained in APCVD at the end of 1960. Data shows that TEOS thermally-activated pyrolysis either in the presence of Ar, or H₂, started at about 500 °C. However, the curve for TEOS-O₂ system shows very unusual behavior at a low deposition temperature. However, the deposition rate was found to be very low for practical use in microelectronic technology.

![Figure 1.13](image_url)

Figure 1.13. Ability of TEOS to react with oxygen at very low temperature as compared to hydrogen and argon (a) (re-drawn using data [304]), and acceleration of TEOS-O₂ reaction with ozone and substrate dependence of deposition rate (“surface sensitivity” effect) (re-drawn from [122]).
However, ozone addition to oxygen [96] was found to accelerate the deposition rate significantly, making this low-temperature deposition applicable for industrial silicon dioxide and silicate glass thin film deposition [106,114,120,122,161]. Moreover, the TEOS-ozone CVD process was found to depend on the substrate material. This feature is illustrated in Figure 1.13(b) for silicon and silicon nitride substrate surfaces. It can be seen that depending on the ozone concentration in oxygen, the difference between the deposition rates on silicon and silicon nitride can reach about 30%, and the deposition rate is faster on silicon surfaces.

In addition, this ozone-based deposition process was found to provide much better step coverage on stepped IC device structures.

The low-temperature thermally-activated TEOS-ozone CVD process was found to be very promising for the semiconductor industry because it was considered as a good replacement of the silane-based chemistry, especially because of the potential absence of the aerosol-related problems.

3.3. Basic Silicate Glass Thin Film CVD Kinetic Features

It was discovered that the phosphorus and boron additives have an important part in the silicate glass film deposition [2,3]. Phosphorus compounds are known to accelerate the oxidation of silicon compounds, reducing the activation energy by a factor of 1.3 to 3. The acceleration is accompanied by a proportional increase in the phosphorus concentration for both PSG and BPSG thin films. This acceleration also degrades the film uniformity and enhances the formation of aerosol by-products. Maximal acceleration (by a factor of 3 to 7) was found with TEOS-based chemistry, namely with TEOS-PH$_3$ combinations. However, it is minimal with silane-based chemistry in any combination with phosphorus compounds. It has also been found that boron compounds tend to inhibit CVD involving silane and phosphine. This feature of silane-based oxidation in the presence of phosphorus and boron compounds is presented in Figure 1.14 using the kinetic time curves of Figure 1.10 in general form. In Figure 1.14, one can see that the introduction of phosphorus compounds into the CVD reactor to deposit PSG thin films causes the change of the SiO$_2$ kinetic curve. The maximum shifts to the shorter $\tau_{\text{max}}$ value and $W_{\text{max}}$ increases. In contrast, in the presence of boron compounds one can see a change of the SiO$_2$ curve reflecting a suppression of oxidation reaction. In this case, maximum shifts to the longer $\tau_{\text{max}}$ value with respect to the SiO$_2$ kinetic curve and $W_{\text{max}}$ decreases.

The author would like to emphasize that similar to the graphs in Figure 1.10, the curves in Figure 1.14 clearly confirm that silicate glass CVD thin film process analysis in a reactor without taking into account real kinetic curves is meaningless. In fact, by placing the only one control substrates just at the same place in the tubular reactor that is indicated as A, B, C, D in the graph will give the wrong kinetic trends, as shown in the top right corner of the graph.

We believe that one of the most important silicate glass CVD features is the differences of the silane-based and TEOS-based kinetic curve behavior after the CVD acceleration by phosphorus compounds. It was found that acceleration of the TEOS-based thin film CVD (whether oxygen or ozone is used as oxidizer) is much more pronounced as compared to silane-base CVD. As an example, about a 5.5 times acceleration effect is clearly demonstrated
in Figure 1.15 [184]. In addition, accelerated reaction clearly reveals the presence of reaction maximum.

Summarizing all of the above, it has been found that phosphorus compounds exert a major influence on deposition kinetics:

- phosphorus compounds accelerate the reaction and shift the time curve toward shorter residence times;
- phosphorus compounds enhance the incorporation of boron into the film, whereas boron compounds inhibit the incorporation of phosphorus. When the oxidation reactions are inhibited by boron compounds, the time curve is shifted toward longer residence times and aerosol by-products are not observed;
- phosphorus compounds also enhance the formation of aerosol by-products (see below).

As for the boron compounds effect, it is significantly less and, basically, can be ignored for major analysis.

Experimental comparison of acceleration effects in different CVD silicate glass chemistry was done by Vassiliev [207,224]. Direct comparison of experimental CVD kinetic time curves with and without acceleration is shown in Figure 1.16. Here the silicon dioxide time curves (presented in Figure 1.12 in general form) were taken as the bases. It is important to highlight that the PSG and BPSG CVD processes taken for comparison provided close enough comparative values of phosphorus content in the films; the latter gave the hard base for comparison.

Data in Figure 1.16(a) show that silane-based acceleration was found to be about 30%, while TEOS-based acceleration was about 5.5 times (see Figure 1.16(b)) re-calculated using the graph in Figure 1.15(a). In addition, a clear maximum close to low residence time values appeared on the accelerated time curve for TEOS-ozone reaction. At the same time, DMDCS-oxygen system, taken as an example of CVD reaction with in-situ acceleration (see Figure 1.12, curve 2) showed a middle-acceleration behavior, of about 3 – 4 times. This comparison clearly demonstrates that the higher acceleration value is a feature of relatively slow SiO₂ CVD using TEOS-oxygen, or TEOS-ozone chemical compounds. Another important feature is that accelerated CVD reactions demonstrate clear maximums on the time curves and the positions of these maximums are close to each other, being near 0.3 – 0.5 s.

A final comparison of additive effects on the CVD silicate glass kinetics is presented in Figure 1.17 [224,276]. These results show that TEOS-based chemistry revealed significantly higher acceleration effects, especially for phosphorus compounds. At the same time, boron compounds were found to accelerate TEOS-based oxidation, but inhibited the silane-based oxidation CVD.

The acceleration effect can be evaluated numerically. For SiO₂ and glasses other than BPSG, k_eff was found to range from 0.3 to 10 cm/s. For the BPSG processes examined, it varies over a narrower range of 1.1 – 2.5 cm/s. It is seen that the silane and the TEOS process have similar characteristics for silicate glasses of similar compositions.
Figure 1.14. Typical changes in kinetic curves for silane-based oxidation (SiO₂) with addition of phosphorus (PSG) and boron (BSG) compounds, causes either acceleration or inhibition of oxidation reaction.

Figure 1.15. Acceleration effect for TEOS-based SA CVD BPSG films vs. total pressure in chamber (re-drawn with simplification from [184]).

This analysis shows that PSG and BPSG thin film deposition kinetics look significantly closer because of the acceleration phenomenon. The kinetic data relating to phosphorus compounds strongly indicate that all CVD processes of BPSG (as well as PSG) are governed by a closely related reaction mechanism. It is believed that it involves free radicals produced by interaction between the phosphorus compound and the oxidizing agent. In explaining these features, it is necessary to note that the oxygen-based oxidation of silane, phosphine, and other phosphorus compounds occurs by the free-radical chain mechanism, see reviewed literature in [3,305]. These findings suggest that the acceleration should be taken to indicate the free-radical chain mechanism of the oxidation. Furthermore, it has been established that the acceleration of oxidation lessens in a sequence: PH₃ → PCl₃ → organic esters of phosphoric or phosphorus acids. This becomes clear because PH₃ oxidation is a well-known example of a typical free-radical (chain-brain) reaction; oxidation of other phosphorus additives studied was significantly poorer. The decrease of the deposition rate along with the
addition of boron compounds implies that the oxidation by the free-radical chain mechanism is being inhibited. The conclusion is supported by a reduced deposition rate when silane oxidation is used, as well as by lower phosphorus content in glasses obtained by adding boron compounds to the source gas. By contrast, the analysis presented in the literature about kinetic data showed that boron compounds accelerate the relatively slow oxidation of TEOS.

Figure 1.16. Comparison of acceleration effects for oxide-based silane and DMDCS compounds (a) and TEOS-ozone compounds (b) (re-calculated from data presented in Figure 1.15).
3.4. **Basic Aerosol Formation Features at Glass CVD**

It is well-known that aerosol (micro-particle) formation is a major problem of the silicon-dioxide and silicate glass thin film CVD processes. Aerosol contamination of thin films is generally unacceptable for microelectronic technology. The technology requirements become harder with the IC technology development. For instance, particles with > 0.1 μm size need to be under systematic control in the IC device manufacturing.

The particle formation problem is very complicated. This is due to a variety of reactors, chemical compounds and process conditions used for the CVD film deposition. Until recently, the reasons and mechanisms of micro-particle formation during the oxidation reactions have not been completely understood. At the same time, micro-particles cannot be considered as something unusual. Aerosol is the solid phase material with a similar composition to the thin films. The difference between them is that thin film is formed on the substrate surface, but particles are formed in the CVD reaction gas-phase. Thus, thin film and micro-particles are both the products of the chemical reaction, but the particles can be considered as undesirable reaction by-products. Therefore, the main goal of the researcher and engineer working in the thin film field is to find the reaction conditions to obtain thin film material without micro-particles.

We would like to stress that some special related research reports were published regarding aerosol formation effects during CVD [218,306-308]. The author’s research results about this matter are presented in [1-3,309]. Basic conclusions made from the research results can be summarized as follows.

1. For any studied silicon-based CVD reaction, the increase of deposition temperatures and deposition pressures were found to enhance the appearance of micro-particles in/on the deposited films. It has been observed for different CVD thin film processes.
that there are some deposition rate values which cannot be exceeded. Above such values, the films reveal micro particle contamination. Generally, these limiting rates are about 1.5 to 2 times higher than the optimized defect-free deposition rates.

(2) For any studied CVD reaction, especially those realized in tubular hot-wall reaction chambers, particle formation effects appear in the reaction area closer to exhaust.

(3) For oxidation CVD processes, acceleration of reaction kinetics causes the enhancement of aerosol problems during the glass film deposition.

(4) To avoid particle formation, it is necessary to decrease the gas phase volume, simultaneously increasing the ratio of the reaction square to the reaction volume (S/V). In LPCVD systems, this can be achieved by placing the substrates with a distance of about 5 mm. between them. In single wafer chambers, the lowest possible spacing between the showerhead and the substrates should be used.

(5) For oxidation CVD processes, the particle formation effect arises in the areas of deposition rate decrease in time curves presented in Figure 1.14.

According to the above listed features, particle formation effects can be characterized by two basic statements:

a) *particle formation effects are proportional to the deposition rate values* (i.e., $T_d$, $P_d$, $[C_{Si}]$, etc) that basically corresponds to the reaction maximum at low residence time $\tau$ values. In this case, fine particles are embedded into the films, changing their appearance (for instance, under the dark field of an optical microscope the surface looks like “polycrystalline”). This is also confirmed by atomic force microscopy measurements of the surface roughness for thin films. In particular, the phosphorus acceleration results in higher surface roughness, and the boron inhibition leads to lower roughness;

b) *particle formation effects are proportional to the residence time $\tau$* that basically corresponds to the reduced deposition rate values. This case was found to correspond to the particles with significantly larger size and particle formation on the substrate surface, on the reactor walls, showerhead, etc. It is necessary to stress that it is very difficult to define the residence time responsible for the large particle formation. Roughly, based on the author experience, it can be designated as the area at high $\tau$ when the deposition rate decreases to the half of the maximum value.

These two cases are represented by a generalized graph in Figure 1.18 as areas with “Fine particles” and “Large particles”. The large particle area is defined as certain $\tau$ corresponded to the $\frac{1}{2} W_{max}$. A solid line represents certain optimized CVD conditions and both substrates positions designated A and B on the time curve provided thin film without particles. Note that wafer positions in the reactor are normally chosen by the experiment and should be close to the time curve maximum. So, from this point of view, both positions A and B presented in Figure 1.18 are acceptable for the film deposition.
It is important to see what will happen when we change these optimized conditions in order to enhance the process productivity. Accelerating the CVD process, either by process conditions, by adding the phosphorus compound or even by plasma gas-phase activation will change the time curve shape to that presented by the dashed line. In this case, a wafer placed in position A will have a higher deposition rate, but it comes to the fine particle area. Sometimes it is acceptable and these thin films can be used, but generally this is the wrong way to “improve” CVD process. At the same time, the wafer in position B after acceleration can get into the area of large particles that is unacceptable for practical use.

Let us illustrate an example above with the comparison of experimental data for TEOS-ozone based silicon dioxide and BPSG thin film CVD in different single-wafer reaction chambers (APCVD, SACVD, and continuous APCVD reactor). This comparison in part was done by Vassiliev [207,224] after re-calculation of the kinetic data published by world-wide researchers [115,122,184] into the parameter of “residence time”. Some necessary numerical data were evaluated based on data taken from the advertisers [310,311]. The final comparison of data is presented in Figure 1.19. It can be seen that with silicon dioxide and BPSG thin films, the CVD processes were realized in a wide range of $\tau$.

The silicon dioxide deposition process was realized in APCVD single-wafer chamber conditions [122] after re-calculation of the drop in the area of the deposition rate decrease with a residence time value of about 0.2 s. At this residence time value, the phosphorus compounds acceleration effect was quite low, not exceeding 30-50%. This area of chemical reaction corresponds to the “Large particle” area. It is necessary to note that the used single-wafer APCVD chamber had a very specific design with wafer “face-down” position in reactor (see Figure 1.7(a)). We believe that this inconvenient design was chosen to provide the possibility of reducing aerosol formation effects using particle sedimentation phenomenon. At the same time, the APCVD continuous chamber with high gas flow passing through a very narrow single injector [115] allows the provision of very high gas velocity or, vice versa – very low residence time. This corresponds to the effective non-particle area of the time curves (see triangles in Figure 1.19). Kinetic time curves that are presented for silicon dioxide SACVD process conditions in a wide range of $\tau$ [184] were found to be quite close to both the above cited APCVD process conditions.

Although they are close for silicon dioxide thin films, these processes differed drastically for BPSG thin films. The value for the maximum in the SACVD BPSG time curve was
evaluated to be about 0.05 s. Note that this CVD process was realized in the single wafer chamber presented in Figure 1.7(b) exactly in the area of $\tau_{\text{max}}$. There were no data published about aerosol particle problems for SACVD BPSG films. Continuous APCVD BPSG thin films data are presented in Figure 1.19 as fixed data points. The residence time for this case was evaluated to be close enough to the maximum in SACVD BPSG curve. Thus, from chemical point of view the conditions for both cited cases were very close to the maximum yield, i.e. deposition processes were well optimized. Note that in the case of APCVD, this low $\tau$ value can be provided by using very large gas volumes. By contrast, vacuum SACVD conditions made the provision of high gas velocity significantly simpler, by reducing the process pressure a few times. Both these examples showed much better CVD conditions for BPSG film deposition as compared to the single wafer APCVD deposition reactor with a residence time value that was about 4 times longer.

This comparison clearly shows the necessity of careful optimization of CVD conditions that can be made on the base of the experimental time curves calculated using the reactor and CVD parameters. In addition, this methodology allows the detection of the CVD process features in order to find proper ways for further process development and optimization.

Figure 1.19. Comparison of acceleration effects for TEOS-ozone BPSG thin films obtained using different tools and deposition conditions (see text for details).