Chapter 8

BPSG FILM COMPOSITION

Silicon content. The referenced CVD methods produced the stoichiometric films without any excess of silicon. This primarily means that the film deposited the excess of the strong oxidizer (O₂, O₃/O₂ mixture) with respect to the silicon-, boron-, and phosphorus-contained reactant mixture. The silicon content could be easily analyzed using optical methods, which showed refractive index values between 1.44 and 1.48 depending on the additive content.

The only method which can cause a slight excess of silicon with respect to the stoichiometry is the PECVD method with the use of a relatively soft oxidizer, such as N₂O [52,53,85,256,288,290]. To overcome this negative issue, the authors of cited papers proposed to add some oxygen additive to the basic N₂O flow in order to suppress the appearance of silicon excess in the film [52].

Boron and phosphorus content. Additives (B and P) concentration in BPSG film was a matter of particular technology requirements. In BPSG thin films, the range of [B] and [P] varied between 2 – 8 wt % each (see Figure 2.1). The total additive concentrations in the films and their distribution within the wafer sample are normally measured in a few points on the silicon wafer with the use of the in-line FTIR method (see Figure 2.2). Unfortunately, FTIR data are not that informative with respect to the additive, because they represent total additive values in the films taken from a relatively large sample area. Using this technique, it is possible to see the total additive content as well as its increase or decrease with respect to the standard (preliminary calibrated) sample.

The SIMS profiling technique is more informative for BPSG films. This method allows the discovery of some additive deviations from the expected uniform distribution (see Figure 2.9(b)). The typical BPSG thin film CVD process can be divided into three phases: process start, film growth and process finish. In terms of additive and oxidizer flows coming to the reaction chamber, the middle period is normally stationary. This indicates a uniform additive distribution within which the film thickness could be expected. However, the additives distribution within the film is uniform if the CVD process has been optimized properly. Some peaks or depletions of the additive concentration can be observed in the film near the film surface, or the substrate surface (see Figure 2.9(b)). The first case corresponds to the process finish phase, when additive compounds are switched off. The second case is the consequence of the process start phase when additive compounds are switched on either separately, or together. The latter is normally the consequence of badly optimized additive injection in the beginning. This can happen, for instance, in the case of unexpected additive flow pulse due to...
the overpressure in the gas manifolds. The second case of intentional additive compounds switching-off was proposed in [109] as a simple solution of undesirable BPSG film moisture absorption phenomenon. Switching-off the additives in the last few minutes of the CVD process allowed the growing of a very thin protective silicon dioxide layer (frequently called “cap-layer”) with significantly reduced additive content. This layer suppressed moisture interaction with the film and enhanced its stability (see more detailed discussion below).

It was found [224] that, in some cases, the behavior of additives distribution in the cap-layer can differ. For example, in SACVD BPSG films (Method 5), the boron concentration decreased much faster than the phosphorus concentration after additives compounds switch-off while depositing the thin silicon dioxide cap layer. In several cases, it was observed that the phosphorus concentration remained stable or increased slightly through that thin cap layer after compound switch-off. This is clearly shown in Figure 2.10(a). These data are in agreement with previous data for APCVD TEOS-ozone BPSG films deposited using Method 4 at atmospheric pressure [171]. Therefore, in accordance with the SIMS analysis, near the film surface of both atmospheric and subatmospheric pressure BPSG films, the phosphorus content is much higher than boron content.

In contrast, PECVD BPSG film grown according to Method 8 did not show a similar behavior (see Figure 2.10(b)). It can be seen that both additive concentrations in the film decreased. This was explained by the lower process pressure during PECVD film deposition. The lower pressure provided a considerably lower “time constant of the deposition chamber” of PECVD vacuum system as compared to SACVD and, especially, APCVD systems (this is analyzed in Part 1 of the monograph). Due to the low time constant, after compound switch-off, the residual concentration of additives in the gas phase is reduced much faster than that of SACVD conditions.

![Figure 2.10. SIMS profiles of boron and phosphorus in as-deposited SACVD BPSG (a) and PECVD TEOS-oxygen BPSG film (b) [224]. Reproduced by permission of ECS – The Electrochemical Society.](image)

Another observed specific feature of SIMS profiles in BPSG films deposited using Method 5, is the higher deviation of additives concentration in SIMS profiles as compared to PECVD TEOS-oxygen BPSG films (Method 8) (as can be seen in Figure 2.10(a,b)). A similar result was shown in [171] for APCVD BPSG film deposited using Method 4. Analysis
of these differences in terms of standard deviations revealed about three to five times higher deviation values for SABPSG films than those values in PECVD BPSG films.

Film anneal at enhanced temperatures was found to cause some additive decrease (1.5 times) in a 200 – 300 Å region near the surface; the highest decrease of additives was found to be after steam anneal of BPSG films. In both cases, this depletion is considered to not be that important.

**Additive state in the CVD glass films.** According to classical chemistry, the complete oxidation of any boron and phosphorus compounds results in boron oxide B₂O₃ and phosphorus oxide P₄O₁₀ (or usually simplified to P₂O₅). Normally, for practical CVD, an oxidizer is used to obtain excess respect to the reactant mixture. There has been no published data regarding the different status of boron in the glass films instead of B₂O₃. Thus, the CVD oxidation product of any boron compounds can be assumed to be the only B₂O₃.

The situation with phosphorus could be different because of many variations with the compounds used. The author would like to highlight one very important aspect of phosphorus analysis in the films, obtained using CVD Methods 1 – 3 [56,83,61] and PECVD Methods 6,7 with the use of N₂O as an oxidizer [52,53,85,256,288,290]. Analyzing the phosphorus state in the films deposited with the use of a strong oxidizer, such an oxygen and ozone-oxygen mixture, most of researchers showed that phosphorus was incorporated in the films in a form of phosphorus oxide P₂O₅ with phosphorus in P³⁺ state. However, depending on the PECVD conditions, phosphorus was found to exist in different forms: such as P₄O₁₀ (P³⁺), P₂O₁₀ (P⁵⁺), PH₃ (P⁺), and phosphorus directly linked to a silicon (P⁰) state. This observation was confirmed by the comparative measurements between the total amount of phosphorus in the films and less than that phosphorus oxide quantity in the films [63]. Using the ion chromatography method, the P₂O₃ additive in the films was detected with the content below 1 wt % [52]. The free phosphorus state (P⁰) detected with the ESCA method as Si – P bond (130 eV) together with P – O bond (134 eV) was also reported in [322].

These different phosphorus states were due to the incomplete oxidation of compounds with different initial phosphorus states. For instance, Robles et al. [161] used (C₃H₆O₃)₃PO as a compound in reaction with TEOS-O₂/O₂ mixture and, checking the content of P₄O₁₀, free phosphorus and P₂O₅ in the films, concluded that the content of the latter two was almost nonexistent. It could be predicted, as long as the possibility of P⁰ or P³⁺ existence in SABPSG films seems to be impossible due to the P⁵⁺ state of phosphorus already in the TEPO compound molecule along with a strong oxidizing (ozone-oxygen mixture) ambient in the reaction chamber.

In summary, it is possible to conclude that careful optimization of the CVD process allows obtaining the stoichiometric BPSG film composition. It is important to note that post-deposition film anneals help to increase the concentration of the P⁵⁺ state in the film. The case of stoichiometric BPSG film compositions will be considered below, because PECVD Method 7 was used relatively rarely as compared to the others.

**Carbon content.** The presence of carbon impurities in the deposited films is an additional characteristic of vitreous materials prepared using the CVD technique and organic compounds. The carbon content was measured by SIMS. Its concentration was uniform within the film depth with a little increase near the film surface that can be explained by the film contact with the ambient.

The average concentration of carbon in SACVD BPSG films measured by SIMS was found to be less in films with a higher phosphorus content (see Table 2.4). For instance, the
carbon concentration in the phosphorus-rich glass films (7 wt % [P] and 3 wt % [B]) produced by Method 5 was uniform over the film thickness. It was approximately three times lower than that in the films containing approximately equal concentrations of phosphorus about 4 wt. % (~ 1.05×10^{19} atoms/cm³ and ~ 3.19×10^{19} atoms/cm³, respectively).

It is necessary to note that thermally activated CVD processes with a relatively large excess of oxidizer with respect to compounds always produced a relatively low content of carbon.

In contrast, PECVD methods were found to cause a problem of IC device damage during its manufacturing known as “Plasma-Induced Damage”, PID [323-326]. High radial charge non-uniformity was found for PECVD systems with diode types of reactors, particularly using SPV/SCA analysis. It was found to depend on the oxygen to silicon compound ratio. Using the SIMS method, it was found that the increase of O₂/TEOS mole ratio from 2 to 40 caused the exponential decrease of carbon content from ~ 9.5×10^{20} atoms/cm³ to ~ 1×10^{20} atoms/cm³ [327]. At the same time, the authors found an almost linear correlation of charge in the range of 0.1×10^{10} до 2.5×10^{10} ions/cm² in the silicon dioxide film with the increase of carbon content from 0.3×10^{20} до 5.5×10^{20} atoms/cm³. As a result of the study, the authors have chosen a O₂/TEOS ratio to be at least 30 that was about 3 times higher than that required according to a scheme of proposed TEOS oxidation reaction.

**Hydrogen content.** Hydrogen was found in the glass films prepared by the referred CVD methods. Generally, the hydrogen concentration is uniform within film thickness. It increases noticeably when the deposition temperature becomes lower than 400 °C. Comparative study of hydrogen concentration in sequentially deposited CVD films used for ULSI technology was performed intentionally in [317]. For one-time SIMS hydrogen profiling, the following films were sequentially deposited in stacked structure: thermal oxide, LPCVD polysilicon (with following boron implant and anneal), CoSi, PECVD silicon nitride layer (PECVD-SiN), SACVD BPSG, PECVD silicon dioxide (PECVD SiO₂), HDP-CVD SiO₂ and PECVD - SiN. Experimental data are presented in Figure 2.11.

It can be seen that hydrogen concentration in as-deposited SACVD BPSG film (Method 5) containing 4.5 wt. % [B] and 4 wt. % [P] was found to be uniformly distributed having an average value as low as 3.0×10^{20} atoms/cm³. This was found to be not higher than that of PECVD silicon dioxide film deposited using Method 8 without additives (about 6×10^{20} atoms/cm³), or HDP-CVD SiO₂ film using Method 9 without additives (about 4×10^{20} atoms/cm³).

After the film RTA at 850 °C for 30 seconds, hydrogen concentration was found to be about 1.3×10^{20} atoms/cm³.

The hydrogen concentration in as-deposited and non-capped SACVD BPSG films stored in clean-room conditions for 3 weeks was found to be increased up to about 3×10^{21} atoms/cm³, reflecting the moisture absorption effect. This observation corresponded to the adequate changes in FTIR spectrum moisture-related areas (see detailed discussion in Chapter 12). Thus, hydrogen can exist in the film either as free hydrogen, or in a hydroxyl group, or in the trapped water.
Table 2.4. Average carbon concentration in SACVD BPSG films ($\times 10^{19}$ atoms/cm$^3$) [224]. Reproduced by permission of ECS – The Electrochemical Society

<table>
<thead>
<tr>
<th>Additives content</th>
<th>As-deposited FA, N$_2$, 45 min</th>
<th>FA, O$_2$, 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 wt % [B] – 4 wt % [P]</td>
<td>3.19</td>
<td>0.92</td>
</tr>
<tr>
<td>3 wt % [B] – 7 wt % [P]</td>
<td>1.05</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Figure 2.11. Hydrogen concentration profile in studied stacked films. Presented at 17th Intertn. VLSI Multilevel Interconnection Conf. (VMIC), 2000 [317].