Chapter 9

BPSG FILM STRUCTURE

In Part 1 of the monograph, we analyzed some aspects of BPSG film growth under a variety of CVD methods and process conditions. It is important to emphasize that the CVD technique is not a usual glass forming technique. Its major feature is the formation of a complete glass structure during film deposition in the additive ranges presented in Figure 2.1. On one side, the CVD temperature is high enough to form the film structure (> 400 °C). However, on the other side the post-deposition anneal in device technology is performed at a lower temperature than that of glass crystallization temperature and there is a trend to soften the anneal conditions. Thus, the as-deposited BPSG structure can be considered as a relatively stable glass structure consisting of Si, B, P, O atoms.

Note that the summary presented in Chapter 8 showed that the concentrations of carbon and hydrogen in CVD glass film are low enough to affect the glass structure. Therefore, these impurities can be simply ignored for glass structure considerations. However, BPSG film properties differ from one glass type to another one due to the difference in CVD features, such as deposition conditions and the chemical compounds used. BPSG as a ternary glass is a complicated glass material.

Therefore, basic glass composition (quantity of Si, B, P, O) is a very important factor strongly affecting film properties. In fact, it was shown that film properties depend on phosphorus and boron oxide concentrations and their ratio in the film.

Despite the active and long application of BPSG films in IC technology, BPSG film structure-related data have been published very rarely. To date, there are only a few summaries about this matter written by the author [2,269,270,276,281]. In Chapter 9, spread related information found in a wide range of literature sources is consolidated. Some data have also been taken from classical glass books and encyclopedias [328-331], as well as from chemical literature [332-338].

The latter helps to understand the basics of the glass ingredient structures. Rare information about boron-phosphorus contained glass compositions was collected basically for bulk glass compositions. This summary helps to explain the peculiarities of the observed BPSG film properties and their dependence on the CVD methods from the structural point of view.
9.1. Brief Review of Silica Structure: Basics and Terms

There are two main classes of solids that are named crystalline and amorphous. In addition to the terms amorphous, solid and glass, other terms are non-crystalline solids and vitreous solids. Amorphous solids and non-crystalline solids are more general terms, while glass and vitreous solids have been historically reserved for an amorphous solid prepared by the rapid cooling of a melt. In fact, according to classical chemistry, glass is considered as a kind of supercooled liquid formed from mixed oxides by the melt cooling method. The difference between crystalline and amorphous solids is the nature of their atomic-scale structure.

The tendency of various substances to form glass was explained by Zachariasen in 1932 [332] in terms of the possibility of specific linking of the elementary structural polyhedra. A continuous random-network glass model that he developed assumed that glasses have a disordered spatial structure. According to Zachariasen, in order for a given oxide $A_mO_n$ to form a glassy solid, it must meet the following criteria: a) the oxygen should be linked to no more than two atoms of $A$; b) the coordination number of the oxygen about $A$ should be small, on the order of 3 or 4; c) the cation polyhedra must share corners only and d) at least three corners must be shared.

In vitreous silica, the elementary structural polyhedron is a SiO$_4$ tetrahedron with a silicon atom in its center. Thus, in amorphous SiO$_2$, each silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms. The nature of bonding in this structure is covalent, bond energy is estimated to be about 434.7 kJ/mol, and the distance between Si and O atoms in tetrahedron is 1.61 Å [338]. All SiO$_4$ tetrahedra are bonded by their vertices by means of Si – O – Si bonds resulting in the formation of a three-dimensional spatial network. Using Myuller’s structural group symbols approach [336], this elementary glass structure is represented by group symbol SiO$_{4/2}$. Therefore, the silicon atom has a fourfold coordination with respect to oxygen and the nature of bonding in this structure is covalent. The network structure is useful to introduce very important terms: short-range order and medium-range order. Atomic positions in a crystal exhibit a property called long-range order or translational periodicity; positions repeat in space in a regular array. In an amorphous solid, translational periodicity is absent, i.e. there is no long-range order. In the glasses each atom has three nearest-neighbor atoms at the same distance (called the chemical bond length) from it, just as in the corresponding crystal. Both crystalline and amorphous solids exhibit short-range order, which is a consequence of the chemical bonding between atoms and which is responsible for holding the solid together. The length of short order (in terms of its radius) is about 1.6 – 2.8 Å. As for medium-range order, its radius is estimated to be 2.8 – 5.5 Å [338]. This term characterizes the structural disordering, particularly, showing the reason of a porosity of a material.

9.2. Brief Review of Boron Oxide and Phosphorus Oxide Structures

This has been illustrated by the use of a simple silica vitreous state structure. Chemical species such as phosphorus, boron and germanium (which like silicon enter into the structure
of the network by forming strong chemical covalent bonds with oxygen atoms) are called network formers. Another chemical species such as sodium and calcium, which do not bond directly to the glass network, are called network modifiers. This case is out of our consideration. It has been mentioned above that in vitreous silica the elementary structural polyhedron is a SiO$_4$ tetrahedron, where the silicon atom has fourfold coordination with respect to oxygen. However, P$_2$O$_5$ and, especially, B$_2$O$_3$ structures are different. Information about boron- and phosphorus silicate glass structures is related to bulk glass compositions. Until recently, there has been no data about thin film glass structures. We believe that the borophosphosilicate glass structure can be understood based on the separate analysis of SiO$_2$, B$_2$O$_3$ and P$_2$O$_5$ structures described for bulk glasses. This allowed us to collect information about these oxides followed by the creation of the ternary glass structure. The latter is believed to be dependent on glass composition. The brief review below is a consolidation of data from [328-338].

The phosphorus oxide network consists of PO$_4$ tetrahedra, where every PO$_4$ tetrahedron is bounded to three other tetrahedra. PO$_4$ tetrahedron has three P – O (1.62 Å) and one P = O (1.39 Å) bonds, and the bond energy is about 339.4 kJ/mol. The elementary structure of vitreous phosphorus oxide, usually represented by chemical formula P$_4$O$_{10}$, is expressed by group symbol 4(OPO$_{2.5}$) [336].

Boron oxide is a significantly more interesting ingredient of BPSG. Considering the physical and chemical properties of B$_2$O$_3$, it is necessary to highlight the following. Many physical properties of B$_2$O$_3$ are sensitive to a small amount of residual water and thermal history. Boric oxide exists as vitreous glass and as two crystalline forms. The vitreous form is a colorless, hard, tough, glass like solid, commonly prepared by the dehydration of boric acid. B$_2$O$_3$ is an excellent Lewis acid: it coordinates even weak basis to form fourfold coordinate borate species. Vitreous B$_2$O$_3$ does not crystallize in the absence of seed crystals or increased pressure. In vitreous boric anhydride, the network is believed to consist of two structural units forming an almost planar or layer-type structure of continuous B – O – B covalent bonds. The distance between layers is about 4.3 Å. The first structural units are random trigonal BO$_{3/2}$ units with a boron atom in their centers, which are linked with neighboring ones by three oxygen atoms. The second one is so-called boroxol (– B – O – )$_3$ rings. The distance B – O in boroxol groups is about 1.37 Å and the bonding energy is about 469.3 kJ/mol. The elementary structure of vitreous boron oxide B$_2$O$_3$ is represented by group symbol 2(BO$_{3/2}$).

There is a certain disagreement over the relative amounts of these two structural units that are due to the presence of residual moisture. It is believed that approximately 2/3 of the boron atoms form the boroxol rings. This network breaks down as the glass melts. It was proposed that above 800 °C, the liquid consists of discrete, but strongly associated, small molecules, conceivably the same monomeric form of B$_2$O$_3$ units that are observed in the vapor phase. The most common crystalline B$_2$O$_3$ form has a hexagonal or α-B$_2$O$_3$ and is crystallized at 200 – 250 °C. A less common monoclinic β-form can be crystallized at high pressure 4000 MPa and 600 °C. The beta-form consists of a highly compact network of BO$_4$ tetrahedra. The acidic character associated with trigonal BO$_3$ groups is thus masked in β-form B$_2$O$_3$. For tetrahedral-type boron-contained glasses with alkali modifiers, the elementary structure unit is designated by group B’O$_{4/2}$. The distance between boron and oxygen atoms in tetrahedron is about 1.48 Å. According to Nemilov [338], combining BO$_{3/2}$ and B’O$_{4/2}$ groups results in the formation of complex groups, such as pentaborate [B$_5$O$_8$], tribourate [B$_3$O$_5$],
Based on a brief review of the literature, the preferable effect of the boron oxide additive and its structure on the BPSG glass structure and properties is undoubtedly expected.

9.3. BPSG Composition and Structure

Considering structures of boron- and phosphorus-contained silica is needed to highlight some important features presented in the literature [333-335]. The studied range of BPSG film compositions (expressed in elemental wt % [B] and [P]) is shown by the data points in Figure 2.1. Normally, the total boron and phosphorus content in the glass films did not exceed 12-14 wt %. The reason of this in case of BPSG films is the following. Englert and Hummel studied bulk SiO₂ – P₂O₅ – B₂O₃ compositions at high temperatures and found the crystallization areas in the diagram presented in Figure 2.12(a). Thus, boron phosphate BPO₄ compound can form at high temperatures in the mixture of oxides.

According to the reference books, boron phosphate is a crystalline material with a tetragonal structure and a sublimation temperature of 1600 °C. Under normal conditions, boron phosphate exhibits a cristobalite structure with BO₄ and PO₄ alternating tetrahedral united by the sharing of oxygen atoms to form a three dimensional structure. BPO₄ can be prepared by different synthesis procedures, in particular, by heating a boric and phosphoric acid mixture at temperatures below 1000 °C [328,331]. According to [337], in the glasses of the BPO₄ – SiO₂ system, crystalline boron phosphate is formed at 950 – 960 °C and silicon oxide does not crystallize in this case. Therefore, a high annealing temperature is a necessary condition for the formation of BPO₄. It should be noted that post-deposition high-temperature BPSG film thermal anneal is a technology requirement to provide glass softening and flow. Therefore, taking into account the BPO₄ formation possibility and BPSG film composition should be carefully optimized in order to avoid BPO₄ crystallization area.

Data presented in Figure 2.12(a) were re-calculated by the author in a convenient form (see Figure 2.12(b)). This graph clearly defines the main area of BPO₄ crystal formation. Comparison of this graph with data presented in Figure 2.1 allows the drawing of Figure 2.13, where all studied BPSG film compositions are plotted together with BPO₄ crystallization area. Most of the studied BPSG film compositions lie quite close to the BPO₄ boundary. This is mainly due to the necessity to provide the best film softening and, therefore, the film planarization on IC device stepped surface, especially at low anneal time, like RTA. However, these compositions were prone to form BPSG defects, either on the surface, or inside the film. This matter will be discussed below in detail in Chapter 13.

Considering data for bulk borophosphosilicate glasses, it is necessary to take into account the results of research performed by Kolesova [316,337]. Using IR spectroscopy, she investigated borophosphate and highly concentrated borophosphosilicate bulk glasses with different compositions. It was shown that for boron-rich compositions, the glass structure consisted of triangles and boroxol groups. In both cases, boron had threefold coordination. It is very important that gradually adding of P₂O₅ to the B₂O₃ or SiO₂ – B₂O₃ mixture resulted in adequate changes to the glass structure. The boron oxide network became broken and the boron changed coordination from threefold to fourfold with respect to oxygen atoms. Eventually, the boron phosphate BPO₄ glass structure (equal concentration of B₂O₃ and P₂O₅) was characterized as a tetrahedral-based PO₄ and BO₄ network.
Similar data were obtained by Aitken et al [284], who studied ternary bulk BPSG samples prepared from mixtures of previously prepared 30 % $P_2O_5$ – 70 % $SiO_2$ and 30 % $B_2O_3$ – 70 % $SiO_2$ glasses. Using the Nuclear Magnetic Resonance (NMR) technique, the authors showed the presence of a very small percentage ($\leq 3\%$) of the total Si in the form of both fifthfold and sixfold coordinated species in the most P-rich glasses. The same glasses revealed an axially symmetric $O=PO_{3/2}$ species, whereas the spectra of B-rich glasses showed only symmetric $PO_{4/2}$ tetrahedra. As boron was progressively replaced by phosphorus, B coordination changed monotonically from fully trigonal to dominantly tetrahedral, with the tetrahedral B fraction ranging from 80 to 95 % for the most P-rich glasses. Overall, the results are consistent with a structural scenario of associated $BO_{4/2}$ and $PO_{4/2}$ tetrahedra comprising a fully polymerized silica-like network for the glasses of intermediate composition. The greater degree of network connectivity was caused by the preferential association of B and P to form $BPO_4$-like groups.
9.4. Differences in BPSG Composition and Structure

Since studies concerning structures for glass thin film materials are absent in the literature, the hypothetical structures of borophosphosilicate glasses are discussed below with allowance made for the data for bulk borophosphate and borophosphosilicate glasses enriched in phosphorus and boron oxides. In this context, the experimentally found that composition dependence of the reactivity for the borophosphosilicate glass films (for example, with respect to the air moisture) is explained by the corresponding dependence of the fraction of boron atoms threefold coordinated with respect to oxygen in the glass network, as well as the specific film structures presented in Figure 1.26.

We select and analyze three important BPSG glass compositions, shown in Figure 2.14, defined as follows: [B] >> [P], [B] ≈ 0.4 [P], [B] << [P].

The first type of glass composition involves borophosphosilicate glass films strongly enriched in boron, i.e. [B] >> [P]. In the structure of monolithic glasses with high boron content, boron atoms are in a threefold-coordinated state with respect to oxygen. The glass structure can contain different groups, such as B₃O₆ boroxol rings and BO₃ triangles. Note that according to the classical literature, pure boron oxide has a layered structure with an interlayer distance of approximately 4.3 Å. For monolithic borophosphate glasses, it was experimentally demonstrated that a gradual increase in the concentration of phosphorus oxide in a batch (and, hence, an increase in the phosphorus concentration in a glass) leads to the destruction of boroxol rings and triangles. In this case, threefold-coordinated boron with respect to oxygen transforms into fourfold-coordinated boron. Therefore, it is reasonable to assume that thin borophosphosilicate glass films enriched with boron should have a different structure due to the formation of the glass structure containing boron in the threefold-coordinated state with respect to oxygen.

![Figure 2.14](image-url)

Figure 2.14. Indication of proposed BPSG structures for three selected BPSG compositions (see text for details) [269]. Reproduced by permission of ECS – The Electrochemical Society.
Based on these properties, the largest structural differences are the feature of CVD Methods 4,5. These methods were characterized by having the smallest effective constant $k_{\text{eff}}$. The formation of these films is described by the two stage scheme of sequential reactions with the limiting heterogeneous stage of consumption of intermediate products of the reaction between tetraethoxysilane, triethyl borate, and ozone. Apparently, these are structures with threefold-coordinated boron which provide a way of penetrating water into the bulk of boron-rich glass films. In particular, this reasonably explains the experimental data regarding moisture penetration in the glass films obtained in [178]. A simple comparison of the effective size of a water molecule (the distance between hydrogen atoms is approximately equal to 1.5 Å) with the hypothetically maximum interlayer distance in the structure of boron oxide (4.3 Å) confirms the consistency of the above assumption.

It is known that according to the Lewis theory, boron oxide is a hard acid and coordinates even soft bases with the formation of structures with a tetrahedral coordination. On this basis, a high reactivity of the boron-rich borophosphosilicate glass films with respect to water vapor could be explained by the fact that threefold-coordinated boron atoms ($\equiv \text{Si} - \text{O} - \equiv$)B in the glass structure serve as acceptors of electron pairs. The water molecules, which are bases according to the Lewis theory, play the role of donors of electrons pairs. However, it is known that water oxygen is not a good donor of electron pairs and cannot form a donor-acceptor bond with boron and transform it into the tetrahedral coordination. Specifically, metaboric and orthoboric acids are the sole products of the addition of water to boron oxide. Therefore, the existence of stable ($\equiv \text{Si} - \text{O} - \equiv$)$_3\text{BOH}_2$ structural groups, in which boron would have a tetrahedral coordination with equivalent bonds between the boron atom and all four oxygen atoms, seems to be unrealistic. Moreover, according to [178], water is weakly bound and tends to migrate from the surface of the glass film into the bulk, i.e., from one boron atom to another boron atom. In this respect, we can assume the formation of a [($\equiv \text{Si} - \text{O} - \equiv$)$_3\text{B}$]$\bullet \text{H}_2\text{O}$ group, in which water exists in a way similar to crystal hydrates.

The introduction of phosphorus compounds into the mixtures of alkoxy compounds and oxygen leads to a multifold increase in the rate of oxidation reactions. This can be characterized by an increase in the effective constant $k_{\text{eff}}$ and to an increase in the effective density of borophosphosilicate glass films. This increase is proportional to that in the phosphorus concentration in the films. A decrease in the absorption of water by borophosphosilicate glasses with an increase in the phosphorus concentration is explained by the simple decrease in the number of threefold coordinated boron atoms with respect to oxygen.

**The second type of glass composition** is the most interesting. It includes glasses characterized by a low reactivity with respect to the moisture at the concentration ratio [B]/[P] $\approx 0.4$. This ratio corresponds to equivalent contents of $\text{P}_2\text{O}_5$ and $\text{B}_2\text{O}_3$ oxides in borophosphosilicate glass. Note that this is close to the BPO$_4$ composition line in Figure 2.14. It is assumed that all boron atoms in the glass are fourfold coordinated with respect to oxygen. The structure of this glass is similar to those of silicon oxide and boron phosphate. It can be represented as a three dimensional random network composed of $\text{SiO}_4$, $\text{BO}_4$, and $\text{PO}_4$ tetrahedra. In PO$_4$ tetrahedra, three bonds are bridging with Si atoms and the fourth bond is the double bond. The structural group of this glass in which boron and phosphorus atoms are linked by oxygen bridges can be written in the following form ($\equiv \text{Si} - \text{O} - \equiv$)$_3\text{OP} - \text{O} - \text{B}(-\text{O} - \text{Si} \equiv)_3$. It is obvious that a glass of this type has a much better ordered structure...
compared to glasses enriched with boron. This implies that the glass of the composition under consideration insignificantly absorbs the air moisture and weakly interacts with it.

The third type of glass composition involves glasses enriched with phosphorus, i.e. [B] << [P]. Phosphate glasses have a structure in the form of a three-dimensional random network comprised of SiO$_4$ and PO$_4$ tetrahedra. The interaction of water vapors with glasses can be described in the same manner as in the above case.

Therefore, in light of proposed BPSG film structure-composition correlations, the properties of the borophosphosilicate glass films studied can be determined by several factors. Among them are:

- kinetic features of the chemical vapor deposition methods, which are responsible for the porosity of the synthesized glass films, as shown in Figure 1.26;
- occurrence of a certain number of boron atoms in the threefold coordination with respect to oxygen in the glass structure;
- total oxide concentration in the glass;
- concentration and sizes of phosphorus oxide clusters embedded into the glass structure.

The heat treatment of glasses at temperatures above their softening point leads to a decrease and disappearance of pores and the incorporation of clusters into the glass structure and their evaporation from the films. As a consequence, after heat treatment at high temperatures, BPSG films prepared by different CVD methods that have identical compositions become similar in their film properties.