Chapter 11

**BPSG Film Flow Capability**

Historically, in multilevel VLSI and ULSI circuit technology, BPSG films are used as a planarized Pre-Metal Dielectric (PMD). The major BPSG film property, employed in integrated circuit technology, is a capability to soften (to flow) when being deposited on stepped device surfaces followed by being heated at enhanced temperatures. This allows smoothening (planarization) of high as-deposited film steps and, therefore, improvement of the quality of a metal film, sputtered over the smoothed BPSG film, see Figure 1.1. Sufficient BPSG film planarization can be achieved at significantly lower post-deposition anneal temperatures, as compared to that of PSG films, either at isothermal furnace anneal or rapid thermal anneal conditions. In this chapter, we briefly describe the basics of the glass flow capability, which are necessary for understanding of BPSG film softening features on device structures. The latter is described quantitatively in Part 3 of the monograph.

### 11.1. Brief Description of Glass Flow Basics

According to classical chemistry, bulk glass is considered as a kind of supercooled liquid formed from mixed oxides by the melt cooling method. The so-called “glass transition temperature” (\(T_g\)) (it is also called “glass transformation temperature”) is one of the major characteristics of bulk glasses. This temperature defines a temperature region where many of the glass properties change significantly. This \(T_g\) temperature is associated with the slowing down of molecular rearrangements in the glass structure during the cooling of glass melt. As an example of \(T_g\) experimental measurement for a bulk glass sample, a thermal expansion curve with \(T_g\) indication is shown in Figure 2.20. The rate of molecular rearrangements is closely associated with viscous flow and \(T_g\) occurs in all oxide glasses at a viscosity of about \(10^{13}\) Poise. The softening point of a glass is the temperature at which it has a viscosity of \(10^{7.6}\) Poise.

It is known that glass viscosity varies exponentially with the temperature:

\[
\mu = \mu_0 \times \exp\left(\frac{E_a}{RT}\right),
\]

(2.1)
where $\mu$ and $\mu_0$ are glass viscosities, $E_a$ is an activation energy, $R$ - gas constant and $T$ is temperature. In many cases, the viscosity in the region between $T_g$ and temperatures corresponding to a viscosity of $10^8 - 10^{10}$ Pouse is better described by the empirical so-called FVT relation [54]:

$$\mu = \text{const} \times \exp\left[ B / T - T_0 \right], \quad \text{(2.2)}$$

whose validity, as well as $B$, $T_0$ and the values of the constant, depends on the length of the approximation interval.

Nassau et al [54] studied a number of glass compositions and showed, that a flow temperature $T_f$ in thin film glass material would be expected to be close to the glass softening point and can be linked to $T_g$ using an empirical equation:

$$T_f = T_g + 288 \pm 16^\circ C \quad \text{(2.3)}$$

### 11.2. Glass Structure Features and Glass Flow Capability

When added to silicon dioxide, the phosphorus, boron, arsenic and germanium oxides decrease the glass transition temperature. Examples of $T_g$ decrease in the boron- and phosphorus-contained bulk silicon dioxide are shown in Figure 2.21(a,b). Boron oxide was found to be the most effective additive, which decreased $T_g$ significantly [54,284].

Analyzing the reasons for additive oxides influence on silica $T_g$ need to mention the following. The strength of the oxygen-central atom bonds in SiO$_2$, GeO$_2$, B$_2$O$_3$, P$_2$O$_5$ is about 418 kJ/mol for all oxides. These values, therefore, do not correlate with the experimental viscosity values for these oxides, shown in Figure 2.22. At the same time, the melting points of the crystalline oxides goes along with the variation in viscosity (1710 °C for SiO$_2$ cristobalite, 1116 °C for GeO$_2$hexagonal, 580 °C for P$_2$O$_5$, and 450 °C for B$_2$O$_3$). This is strong indication that the additive oxide structure is a very important factor affecting glass viscosity.

A brief review of the information regarding vitreous oxide structures allows us to make the following conclusions. In vitreous silica the elementary structural polyhedron is a SiO$_4$ tetrahedron with a silicon atom in its center. These 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. The same structure is in GeO$_2$. However, structures of P$_2$O$_5$ and, especially, B$_2$O$_3$ are different. In the phosphorous oxide network, every PO$_4$ tetrahedron is bounded to three others, because the fourth tetrahedron vertices is P = O bond. Therefore, the lower viscosity of P$_2$O$_5$ is due to its structure. In vitreous boric anhydride, BO$_3$ triangles with a boron atom in their centers are linked with neighboring boron atoms by three oxygen atoms. As a result, an almost planar structure of continuous B – O – B bonds is formed. In this layer-type structure, approximately two-thirds of the boron atoms form the so-called boroxol groups. Thus, the linked-ring structure of boron oxide is believed to be the reason for the low viscosity of this oxide.
As a general sequence of the above consideration, glass viscosity is linked to glass structure. During the addition of the oxides B$_2$O$_3$ and P$_2$O$_5$ to SiO$_2$, the silica network becomes broken resulting in local distortions of the structure and a lowering of the viscous flow of glass. Undoubtedly, oxides with strongly different structures from SiO$_2$, such as B$_2$O$_3$,
are supposed to be the most effective in distorting the SiO₂ structure and, therefore, in lowering the glass flow temperature.

11.3. APPLICATION OF BULK GLASS PARAMETERS TO GLASS THIN FILM

At the first glance, borosilicate glass can be considered as the best flow-able glass film to solve planarization issues in integrated circuit devices. However, the P₂O₅ additive is necessary to keep gettering properties of a silicate glass with respect to alkaline metals. Thus, both boron- and phosphorus-containing glasses were chosen to serve as the best option for flow-able thin film glass material applicable for IC technology [49,50,54,55].

In this section, we discuss the validity of the term T₉ for CVD glass films [2]. FTIR data showed that a more or less perfect glass structure of thin film is forming at the deposition temperature being used. Following the discussion of BPSG film deposition scheme in Figure 1.25, a formation of glass structure can be assumed to occur in the gas-phase through the formation of reaction intermediates followed by their diffusion to the substrate surface and film built-up. In fact, an analysis of the FTIR spectra of as-deposited and annealed films does not show any significant structural differences, which would confirm serious changes of glass structure and, therefore, glass properties at post-deposition heating.

Using this approach, T₉ and T₇ values can be evaluated for practically used BPSG film compositions, as shown in Figure 2.23. Glass composition is expressed as the total additive concentrations in elemental wt % assuming three simplified possible additive ratios in glass film, namely [B] > [P], [B] = [P] and [B] < [P]. Calculated data points reflect bulk glass film composition and for these glass compositions T₉ represents a certain temperature, where many bulk glass properties change significantly.

Considering thin film glass materials, it can be seen that most of the known thin film CVD methods are performed at deposition temperatures T₉ of about 450 °C. This is significantly less than that of T₉. After deposition, BPSG films require additional heating (anneal).

High temperature post-deposition BPSG film thermal anneal corresponds to T₇ conditions, as shown schematically by the dashed arrow in Figure 2.23. In contrast, low thermal budget anneal, especially at RTA conditions, is expected to be closer to the calculated T₉, as shown schematically by the solid arrow in Figure 2.23. The low thermal budget BPSG anneal conditions used in device technology in recent years in most cases fall into the gap in between glass transition temperature T₉ and glass flow temperature T₇. In this case, post-deposition film anneal at temperatures higher than T₉ causes a densification of film, but does not change the film composition and bonding significantly. Therefore, implementation of bulk glass characteristic T₉ to CVD glass films characterization is done for an artificial reason.
Figure 2.22. Viscosity vs. reciprocal temperature for different glass-forming oxides [54]. Reproduced by permission of ECS – The Electrochemical Society.

Figure 2.23. Temperature diagram for BPSG films: deposition temperature $T_d$, calculated glass transition temperatures $T_g$ according to [54], and calculated flow temperature $T_f$ for the same glass film composition. Arrows indicate assumed high (dashed) and low (solid) thermal budget anneal conditions after film deposition.