Chapter 1

**BRIEF HISTORICAL OVERVIEW OF BPSG THIN FILM RESEARCH**

Inorganic materials are used in solid-state technologies in the form of thin films with thickness in a range from a few tens of angstroms to a few micrometers. These films are created on the surface of a semiconductor or insulating substrates using a variety of CVD techniques. The first most comprehensive monograph covering many aspects of thin film CVD was published by Powell, Oxley, and Blocher in 1966 [5].

Generally, silicon-based films such as silicon dioxide and silicate glasses, polycrystalline silicon, silicon nitride, as well as metals and metal silicides, have become the basic thin film materials in IC technology [6-14]. A variety of tools, chemical compounds and deposition conditions have been investigated for thin film deposition over the last 40 years. Some aspects of film deposition techniques, thin film properties and application issues in microelectronic technology have been summarized in a number of monographs, reviews and surveys published in the last part of the 20th Century [6-47].

Silicon dioxide-based thin film materials revealed some specifically important material properties such as insulating properties and gettering properties with respect to alkali ions (phosphorus-contained silicon dioxide). Phosphorus- and boron-contained silicon dioxide thin films also revealed a capability to soften at enhanced post-deposition temperatures. These features presented a reason why the silicon dioxide-based thin films have been chosen as a base for silicon IC technology. These dielectric films are widely used in microelectronic technology for shallow trench isolation, spacer isolation, dielectric isolation between metallization layers, final device passivation, etc. These dielectric films are deposited using a variety of chemical compound combinations and CVD methods, such as atmospheric, subatmospheric, or low-pressure chemical vapor deposition (APCVD, SACVD, and LPCVD, accordingly), and plasma-enhanced (PECVD) and high-density plasma (HDP-CVD) deposition.

Intensive studies of thin P\textsubscript{2}O\textsubscript{5}-containing insulating phosphosilicate glass films were stimulated by the rapid development of microelectronic technology, and the advent of very large-scale integrated (VLSI) circuits followed by ultra large-scale integrated (ULSI) circuits [7-10]. These films were considered for use in electronic technology for two basic purposes: (a) as an IC device passivation dielectric, and (b) as a “Pre-Metal Dielectric, PMD” for the separation of IC transistor level from the first metallization level [15-20]. Dielectrics like PSG
thin films with elemental phosphorus content within a few percents revealed gettering properties against undesirable alkali metal diffusion from ambient into the transistor structures. Being thermally treated at high temperatures caused the film flow and PSG films were found to provide a smoothing (planarization) of the dielectric surface and rounding of the contact hole top edges. Planarization was found to be necessary in IC device technology due to the non-conformal metal sputtering on the sharp device steps (see Figure 1.1(a)) and, therefore, metal line imperfection on the side walls of IC device structures (see Figure 1.1(b)). Thus, flow-able dielectrics provide a reliable multilevel metallization system formation.

In the mid-1970s, PSG films were used as PMD with about 1 μm thickness and an elemental phosphorus content (C_p) up to 13 wt % (about 30 wt % P_2O_5). PSG films were planarized by viscous flow during a thermal heating of the semiconductor structures covered with glass films. The PSG flow temperature in microelectronic technology was as high as above 1000 °C. This temperature was not applicable for some types of VLSI devices, which required a significant reduction of thermal treatment conditions (frequently called “thermal budget”) in order to minimize lateral and vertical dopant diffusion in silicon substrate. Furthermore, the phosphorus oxide in the film was found to react with the ambient moisture to produce orthophosphoric acid (H_3PO_4). This acid attacks the aluminum metallization causing severe corrosion of the latter [8–10]. As a result, highly P_2O_5 concentrated PSG thin film application in microelectronic technology as PMD material was restricted by the revealed film disadvantages. At the same time, BSG films were rarely used in semiconductor technology.

In the early 1980s, borophosphosilicate glass (BPSG) was proposed as an alternative PMD film. BPSG thin film was introduced in VLSI circuit technology in 1982, when Ramiller and Yau [49] showed some BPSG film advantages over the traditionally used PSG thin films. The same year, the first detailed paper by Kern and Schnable [50]) appeared that was devoted to BPSG film synthesis, composition, properties, and applications in VLSI devices. The proposed BPSG films contained up to about 30 wt % B_2O_3 and P_2O_5 taken together or expressed in elemental content 3 – 6 wt % B and 3 – 7 wt % P, or expressed in oxide content 9.6 – 19.2 wt % B_2O_3 and 6.9 – 13.8 wt % P_2O_5. With about two-thirds of the P_2O_5 replaced by B_2O_3, the problem of VLSI aluminum metallization corrosion was overcome.

In addition, the flow temperature of BPSG films was greatly (by a few hundreds Celsius degrees) reduced compared to PSG films, providing good film planarity and smoothing the contact hole top sharp edges (see Scanning Electron Microscope (SEM) example photos in Figure 1.1(c-f)). The latter feature made BPSG suitable for use with short-channel and shallow-junction transistors and with radiation-hardened VLSI.

Note that despite the fact that BPSG films were first employed in IC with minimum feature size over 1μm, they are also compatible with IC technologies well below that level, such as ULSI technology.

However, due to ULSI device complexity, additional Chemical-Mechanical Polishing (CMP) is used in technology to planarize BPSG PMD films. A simplified sketch of the device structure in Figure 1.2 shows the implementation of glass thin films in ULSI technology.
Figure 1.1. Scanning Electron Microscopy images of polysilicon step covered with glass film (a), metal line imperfection (severe thinning) on the bottom corners of the vertical glass side walls (b), crossing polysilicon lines covered with as-deposited (c) and thermally-flowed (d) BPSG films, and contact holes in as-deposited (e) and thermally-flowed (f) BPSG films on silicon dioxide underlayer that does not flow.
Figure 1.2. Simplified cross-sectional sketch of ULSI structure (not in the scale). Definitions: 1 – silicon substrate; 2 – shallow trench isolation areas; 3 – source-drain doped areas in substrate; 4 – thermally grown gate dielectric; 5 – gate; 6 – spacer; 7 – tungsten plug; 8 – Pre-Metal Dielectric (PMD), made of phosphosilicate glass (PSG) or borophosphosilicate glass (BPSG); 9 – 1st metal layer; 10 – Inter Metal Dielectric (IMD); 11 – 2nd metal layer; 12 – PSG passivation layer; 13 – silicon nitride passivation layer; 14 – contact area.

The first promising results enhanced world-wide BPSG-related research works followed by intensive patent and paper publications during the 1983 – 1989 period. Historically, this time frame could be defined as the first period of BPSG investigation. The related papers are listed in references [51-98] in chronological order. The maximum publication activity took place between 1985 – 1987. During the first years of the film study, some important BPSG-related topics were covered while searching for the optimized glass compositions applicable in the microelectronic technology. They included: a variety of the film deposition aspects (such as type and characterization of the deposition tools, CVD methodology, chemicals characterization and applications, CVD process parameters, etc.), film property characterization (including flow capability at post-deposition anneal temperatures higher than 900 °C, film devitrification and defect formation issues), precise boron and phosphorus concentration analysis, etc. As a basic result of these studies, a suitable BPSG film composition for VLSI device technology was described as a composition with less than about 8 – 10 wt % of elements (or 25 – 30 wt % of P$_2$O$_5$ and B$_2$O$_3$ totally). The first detailed survey of BPSG film publications was performed by Dukhanova, Vassiliev and Veretenin in 1988 [93].

The new research impetus for BPSG film study was stimulated by a number of principal changes in integrated circuit technology and manufacturing. First, it was due to the trend of
the wafer diameter increase from 100 to 150, followed by an increase to 200 mm. This trend pushed CVD deposition techniques from a multi-wafer CVD tool design to different single-wafer CVD tool designs. Secondly, the appearance of VLSI and ULSI circuits with sub-micron technology nodes enhanced issues of CVD film step coverage and gap-fill.

A second period of BPSG investigation started in 1990 (with the maximum publication activity corresponding to the years between 1993 and 1997). BPSG-related research and technology publications were significantly wider and deeper. They are shown in [99-241] in chronological order until 1999. The second survey of BPSG thin film publications was published by Vassiliev in 1998 [207]. The highest patent activity in BPSG-related areas (deposition methods, tools, compounds, film application, etc.), was found to correspond to the years between 1990 and 1997, when about 50 US patents were published (as compared to about 10 patents published before 1990) [207].

The publications of the previous decade were devoted to the deep analysis of BPSG film deposition, properties, and quantified modeling of gap-fill and flow on the device structures, analysis of specific properties of PECVD films, details analysis of production processes, new applications of BPSG films, etc. These publications are listed as references [242-291] in chronological order. A couple of brief BPSG thin film reviews were published by Vasilyev in the middle of the first decade of the 21st Century [276,281].

When analyzing the BPSG publication history, it can be seen that the research activity was followed by the appearance of new BPSG deposition methods. CVD methods of BPSG thin film deposition were the initial push for appearance of new data. The most important milestones of BPSG thin film CVD methods are plotted in the diagram in Figure 1.3 in chronological order.

In Figure 1.3, it can be seen that the most CVD methods were realized at a low deposition temperature (around 400 °C). Important changes in the BPSG film development can be definitely linked to the changes in the chemical compounds used for BPSG thin film CVD: (Silane + O₂) → (TEOS + O₂) → (TEOS + ozone). This was mostly due to the inherent ability of hydrides to form particles during oxidation reactions because of the chain-brain reaction mechanism. Obviously, particle formation phenomenon during thin film formation was in contrast with the IC device-scaling trend. Therefore, the necessity to search for proper compounds to reduce (or exclude) the defect formation processes during the film deposition, become clear. This difficult task was solved by using TEOS-chemistry: first by oxygen oxidation at the middle-temperature range followed by ozone oxidation reaction at low temperatures.

After a detailed analysis of publications, the author has selected nine important BPSG CVD methods, which were realized earlier or later as the industrial deposition processes using the designated industrial tools. These methods will be detailed in the following chapters. However, it is important to emphasize that the most important issue of this monograph is not only analysis of published BPSG-related publications, but also the generalization of the data that are obtained in order to establish a strong interrelation of CVD methods, BPSG material film composition, structure, and properties.

In the diagram in Figure 1.3, we also show two BPSG formation methods which are not CVD-related. The first one is by boron diffusion from BN wafers at high temperature [65] and the second one is by sol-gel method from organic ethers spin-on followed by the film baking [119]. Both these methods will not be analyzed below.
Figure 1.3. A chronology of BPSG thin film CVD method appearance. Definitions: LT - low temperature, MT – middle temperature, HT – high temperature. Silane (SiH₄), represents hydride-based chemistry, TEOS – tetraethylorthosilicate, Si(C₂H₅O)₄, represents organic ethers-based chemistry. References in the diagram indicate the first publications regarding the method.