Chapter 18

**BPSG Films in Electronic Technologies**

BPSG pioneer introduction as an IC production process dates back to 1980 and to RCA (USA). The moving force of the film implementation was the substantially lower temperature of the film flow as compared to PSG films used in IC manufacturing as a PMD material. This was required to produce specific contours in PMD films in advanced devices with short-channel lengths and shallow junctions to minimize the lateral and vertical diffusion of dopants. The fabrication of ICs for use in environments that may contain high levels of radiation also required that processing be done at temperatures considerably lower than those used for the production of commercial integrated circuits. Low process temperatures were also desirable to minimize process-induced crystallographic damage, unwanted impurity diffusion, and distortion effects. With BPSG as a PMD, it was found possible to define processes with a maximum wafer temperature during processing as low as 850 °C. This reduction allowed using BPSG technology for applications that ranged from commercial CMOS circuits in plastic packages to high-reliability, radiation-hardened, short-channel bulk and silicon-on-sapphire (SOS) circuits [50].

BPSG film has now become a routine PMD material. As shown in the previous part of the monograph, BPSG thin films appears to have all of the appropriate physical, chemical, mechanical, and electrical properties that make it suitable for use as a dielectric material in IC technology. BPSG film deposited by all studied CVD techniques exhibited undoubtedly good dielectric properties being studied with “classical” techniques (see Chapter 7) that made them to be an attractive isolation material for device applications.

For a number of applications, BPSG films exhibited properties that made them more attractive than films of the PSG material. From the beginning of their appearance in 1982, BPSG films were considered for use in VLSI and ULSI applications based on a few types of physical and chemical properties:

- lower flow (fusion) temperature PMD material;
- gettering properties;
- moisture absorption effect;
- lower chemical etch rate in ammonium fluoride-buffered hydrofluoric acid solutions;
- lower as-deposited tensile stress;
- lower-temperature doped-oxide diffusion sources.
During a long period of the film studies and employment in the IC technology, the only PMD BPSG application as a lower fusion temperature glass material undoubtedly got widespread use. All of the selected directions of BPSG film application reflect some specific film features, which can be realized in other precision technologies. In this regard, these features are briefly discussed in this Chapter.

### 18.1. BPSG Films as Pre-Metal Dielectric in VLSI and ULSI Circuits

**General considerations of BPSG film applications.** The primary application of BPSG is as a low-temperature flow-able PMD (see Figure 1.2). It is used to ensure adequate metal coverage over steps and into contact vias so that metal discontinuities or local regions with thin metal over steps do not occur. In many applications, two flow (fusion) processes are used: one to smooth the surface topography over steps such as those of a polysilicon gate (called “flow”); and a second, often called “reflow”, to taper contact openings made through the fused ULSG layer. For these applications, it is important to control the top contour of the flowed glass film. In general, the intent should be not to planarize the surface completely, but to taper and soften sharp step sand edges. In circuits of relatively low density, some tendency toward planarization during the first BPSG film flow can be tolerated, but in high-density circuits more precise control of BPSG film contours is required. In recent years, BPSG planarization needs became less necessary due to the implementation of sub-half micron device technology as a Chemical Mechanical Polishing technique. Nevertheless, the BPSG thermal flow process is still in use because it is necessary to fill the narrow gaps between neighbor device elements to eliminate the voiding issues.

The choice of BPSG film composition is determined primarily by temperature limitations of the IC device technology. For example, in the case of processes used for the fabrication of radiation-hardened CMOS circuits, wafer temperatures after growth of the gate oxide were typically kept below the growth temperature of the oxide. For example, a glass composition was selected to permit significant film flow ability below 900 °C in the RCA hardened CMOS/SOS devices [50]. In general, practical considerations suggested the use of the composition with the highest flow temperature that was compatible with the process. As the composition of BPSG was adjusted to lower the flow temperature, a decrease of the film stability or an increase in defect density tended to occur. To decrease this inherent BPSG film property, so-called SiO₂ “cap-layer” with very thin (30 – 100 Å) film thickness deposited in-situ immediately after BPSG film deposition is used, especially for highly additive-enriched BPSG films.

For a typical application of BPSG as a PMD layer, a common approach to the selection of a glass composition was based upon the achievement of an adequate flow in 30 min at the maximum usable temperature. The first flow was normally done in a dry or steam ambient, and the second flow was performed either in nitrogen or in a sequential process, that involves both dry oxygen and nitrogen.

Normally, BPSG films were used in IC device technology as a part of PMD stacked dielectric. To prevent boron and phosphorus diffusion from BPSG films into the gate region, the film was usually used with so-called “barrier” or “liner” dielectrics. In most cases, this
dielectric was 500 – 1000 Å silicon dioxide film. It was deposited using any known CVD technology, for instance, TEOS pyrolysis, PECVD TEOS oxidation, TEOS oxidation with ozone-oxygen mixture and so on. For convenience, these barrier oxides were deposited in the same reactor, with the same chemical compounds, and at the same temperature mostly using PECVD processes to obtain the best liner film density.

However, PECVD methods, giving the best film quality in terms of film density, provide very non-conformal film deposition on the device steps (see Chapter 4 of the monograph). In such a case, in the sub-quarter micron device elements all shapes of the narrow gaps between gates transform into the re-entrant shapes. BPSG film deposition on the re-entrant structures covered with liner oxides enhances the voiding issue. Therefore, more efforts to optimize the film composition and film anneal conditions are required to eliminate this issue. Another issue with PECVD liner films is plasma-induced damage that can be seen, particularly with the use of SCA techniques. To optimize net charge value within the wafer, careful optimization of the PECVD liner process was necessary [343].

In addition to silicon dioxide under- and cap-layers used in combinations with BPSG films, IC technology development required the use of a thin dielectric layer of low etch rate beneath PSG films. Such layers, called “etch-stop layers” (ESLs), were made best with silicon nitride. This material was produced mostly by reaction between silane and ammonia in plasma at about 400 °C. A major drawback with this process was that the hydrogen content in silicon nitride films was about two orders of magnitude higher than in BPSG (see, for instance, data in Figure 2.11). Hydrogen diffusion under thermal annealing is thought to degrade the performance of metal–oxide–semiconductor transistors, as it should enhance boron migration from the gate through the gate oxide [344]. For this reason, interest was developed in high-density-plasma processes, which did not use ammonia [345].

Finally, there were a few attempts to use stacks of BPSG films, in which additive content and, therefore, flow temperature were different in the range of 50 – 100 °C [346]. The top film was considered to be less enriched with additives as compared to the internal layer. However, two- or three layer BPSG stacks are more overcomplicated than useful. In fact, it is very difficult to control repeatability of the process, especially in terms of additive content and their distribution within the wafer. As a result, practically BPSG film stacks did not find any reasonable application in device technology.

**Furnace anneal vs. RTA.** In addition to the selection of the appropriate BPSG composition, the conditions used for the film flow can be adjusted to optimize the final contours of a patterned PMD film or to achieve proper gap-fill. As described earlier, parameters such as temperature, time, film thickness and step coverage, as well as anneal gas ambient and pressure, can be used to influence the flow of a glass. Anneal temperature and time can to some extent be traded-off. In this regard, either furnace isothermal, or rapid thermal anneal, can be selected to be sufficient to meet the device and BPSG film requirements. It is necessary to notice, that excess flow during the first film flow can make the etching of contact holes difficult and uncontrollable since the thickness of the glass layer can vary in the region of the contact to be opened. In the case of a second flow (reflow), which follows the etching of contact openings, very little transport of glass is desired. The top edge of the contact opening should be simply rounded. Details of the film flow at both used film anneal conditions, cross-sectional images and calculations of BPSG film flow on device steps can be found in detail in Chapter 15.
The other major parameter that could be conveniently varied is the ambient used for the flow processes. It was found that for a given glass composition, the lowest flow temperature (down to about 50°C) occurs with a steam ambient. However, film flow under oxidizing conditions may not always be possible or desirable, especially during reflow of the glass after contacts are opened. It should be clear that flow and reflow characteristics of the glass could be affected also by the presence of the SiO₂ cap-layer, which can either suppress or enhance the flow ability of the glass depending on its history (see Chapter 15).

All of the above was linked to the flow characteristics of the glass films. There was no information regarding the anneal effects on device characteristics. The only paper [141] was devoted to an anomalous threshold voltage shift of MOSFET under RTA BPSG flow and reflow. The observed shift was attributed to the induction of a great amount of donor-like states in the SiO₂/Si interface and explained by the thermal strain induced as a result of a very high RTA ramp rate. Post RTA furnace anneal helped to eliminate this effect. Unfortunately, there was no indication about the particular BPSG film deposition process and film properties.

**Application of CMP technique for PMD BPSG films.** For IC devices at feature size of 0.35 um and below, BPSG film global planarization across the whole chip is needed to improve the limited lithography depth-of-focus and increase the yield of metal interconnect. Chemical Mechanical Polishing technology was recognized as one of the most important technologies to achieve global planarization [347]. There were a few papers published regarding BPSG film CMP and their basic results were similar [147,200]. An example of the CMP technique application for BPSG films deposited using Method 5 is briefly described below. The effect of BPSG additive concentrations on the CMP polishing rate was studied using identical process conditions. BPSG films were thermally annealed at 750 °C for 45 minutes.

The experiment was done on an Ebara's EPO213 dual-head chemical mechanical polisher with integrated cleaning stations. Eight inch silicon wafers were used. Rodel's ICI000/Suba IV stacked pads and ILD1300 ammoniated silica slurry were used for the polishing. The pad conditioning method and stable polishing process for TEOS oxide was described elsewhere [200]. It was found that the polishing rate and uniformity of the BPSG film were much higher than those of TEOS oxide when the optimized polishing parameters for TEOS oxide were used. The higher CMP rate resulted in higher wafer-to-wafer variability, which agreed with data reported by Stamper et al [175]. With optimized CMP process parameters, a polishing rate of ~2600 A/min with less than 5 % uniformity was achieved for BPSG films with 4 wt % of boron and 4 wt % of phosphorus.

The polishing rate increases with both boron and phosphorus concentration. The phosphorus was found to have a slightly stronger effect on the polishing rate than boron. The polishing rate of BPSG as a function of total additive concentration (in wt %) is shown in Figure 3.27. The polishing rate increases almost linearly with total boron and phosphorus concentration in the range of concentration studied. A possible mechanism for the increasing of the polishing rate with additive concentration assumes the difference in additive structures with respect to the silica structure. Additives created dangling bonds in the oxide and, thus, weaken the structure of the oxide network with the increase of additive content. Weakening the structure of oxide films may allow the additive oxide to dissolve faster in the high pH silica slurry and therefore result in a higher polishing rate.
18.2. BPSG FILM GETTERING CAPABILITY

The gettering capability of BPSG films is due to a fairly high concentration of phosphorus oxide, a well-known getter for alkali-metal ions. It was demonstrated in experiments using the $^{22}$Na isotope [50,56]. The element was introduced by applying $^{22}$NaCl to the film surface or by ion implantation, followed by thermal processing at 430 – 500 °C. The distribution of sodium indicated that its ions were retained by a gettering mechanism rather than a barrier one. A similar mechanism was identified in PSG films, but these showed a smaller amount of gettering, as evidenced by a larger proportion of sodium ions escaping retention.

18.3. BPSG MOISTURE ABSORPTION EFFECT

Chapter 12 summarizes a large amount of data devoted to the inherent BPSG film property – moisture absorption from ambient. This effect happens at the beginning of the as-deposited film exposure to the air followed by defect formation on the film surface. In Chapter 16, the author considered an approach for quantitative optimization of BPSG film composition. This approach allows obtaining a defect-free film composition during a convenient time delay of 24 hours after film deposition. According to Kern et al [50], as-deposited BPSG films should never be exposed to corrosive or aqueous compound solutions at elevated temperatures. This constraint is due to the boron and phosphorus oxides leaching from the film, similarly to the other CVD films of silicate glasses, such as PSG. BPSG films were recommended to be stored in a dry ambient until they can be flowed.

Hot-carrier-induced MOSFET degradation depends strongly on the quality of the gate oxide. This quality is affected by both the fabrication process and the materials covering the gate oxide. In general, insulating materials easily inject water molecules into the gate oxide because their hygroscopicity is high enough to absorb moisture from ambient. Thus, based on common sense, the moisture content in the PMD material is supposed to be as low as possible.

The authors [176] studied water-related hot-carrier degradation effects caused by BPSG films (Method 1, APCVD) using thermal desorption spectroscopy (TDS) to study quantities and configurations of water molecules in the films. In addition, they used a BPSG film containing deuterium-substituted water to evaluate the behavior of water in interlayer dielectrics. This BPSG film was deposited using deuterium-substituted alcohol in addition to the compounds used for CVD. Deuterium was used to distinguish the incorporated water molecules from those absorbed after the film growth.

Analyzing TDS spectra, BPSG film was found to store a larger amount of water after firm deposition as compared to silicon dioxide films, used as PMD material in parallel. It was expected that the water-related hot-carrier degradation occurs more easily in BPSG samples than in SiO$_2$ samples because the amount of water reaching the gate oxide should be greater in the BPSG samples. Contrary to expectations, there were no differences between BPSG and SiO$_2$ samples found. Moreover, hot-carrier-induced degradation was found to be smaller in BPSG than in SiO$_2$ PMD. These results suggest that the degree of hot-carrier degradation did not necessarily depend on the amount of water contained in the PMD. Although BPSG films
contained more water than SiO$_2$ films, water-related hot-carrier degradation in BPSG devices was superior to that in SiO$_2$ devices. Eventually, the authors came to the conclusion that the hygroscopic BPSG film during film deposition caused the diffusion of water molecules into the underlying oxides. However, after deposition water re-absorption from the underlying oxides takes place and BPSG film acts as a desiccating agent that pumps water molecules out of the top gate and field oxides, thus reducing undesirable effects.

Figure 3.27. Chemical Mechanical Polishing removal rate as a function of total additive content (in elemental wt %) in thermally annealed BPSG films [200].

18.4. BPSG FILM IMPLEMENTATION IN LOW-ETCH RATE APPLICATIONS

The effect of the decrease of BPSG film etch rate in buffered hydrofluoric acid solutions was used for express-control of the boron content in the film. In such a case, it is necessary to calibrate the etch rate values, performed preferably under fixed isothermal conditions (for instance, 25 °C), using a standard analytical technique. The same approach, but the film dissolution in so-called P-etch solution, can be used for express-control of the phosphorus concentration in BPSG films. It is known that this solution is very sensitive to the phosphorus concentration in glass films [18,50]. Using both solutions and calibration curves, which are shown, for instance, in Figure 2.17(a,b), it was possible to realize the immediate evaluation of both additives in BPSG films.

The etch rate of BPSG films in buffered hydrofluoric acid solutions can be comparable to that of SiO$_2$ films, and this feature can be desirable for certain applications. Typical etch rates for as-deposited and thermally annealed (i.e. densified) BPSG films deposited using Method 1 are listed in Table 2.6, together with those for SiO$_2$, BSG, and PSG films for comparison. More details of BPSG film wet etch-related issues can be found elsewhere [159].

The etching of glass films and SiO$_2$ films in both gas- and liquid-phase mixtures containing HF can be catalyzed by water [157,158]. Insufficient water to initiate the etching reaction produces an induction period which can be used to selectively etch glass film relative
to SiO₂. It was found that additives in glass films also enhance the etching reaction by producing low volatility etching products which trap water and may directly catalyze the reaction.

Normally, dielectric films used in device technology are etched using plasma-activated, or so-called “dry methods”. In this case, the dry etch rate was found to be practically equal for SiO₂ and glass thin film. For instance, we found a similar dry etch rate value of about 3600 Å/min for annealed BPSG films deposited using Methods 5 and 8, and as-deposited HDP-CVD SiO₂ and PSG films. This means that PECVD etch rate will be similar through the any SiO₂-based film stacks no matter it includes BPSG films or not.

18.5. BPSG USE AS LOW-STRESS FILM

Low-temperature CVD films of SiO₂ tend to be in tensile stress as deposited. The addition of phosphorus oxide or boron oxide to CVD SiO₂ films is known to decrease tensile stress, thus permitting use of relatively thick films on Si without cracking. However, since CVD films with higher phosphorus concentrations can result in Al metal corrosion in plastic-encapsulated devices, the maximum phosphorus content that can be used in low-temperature-deposited (400 °C) CVD phosphosilicate glass films over Al metal is approximately 4 wt % [P] [18]. Thus, it was expected that the lowering of the phosphorus content can be achieved by the use of the boron additive in the film. As-deposited at 430 °C CVD BPSG films are in very low tensile stress in the range of 9×10⁸ dyne×cm⁻². Thus it may be considered for applications in which low film stress is desirable. Examples of such applications can be as follows: IC device structures with thick (> 5 μm) dielectric films; passivation layers in device structures with thick metallization layers (> 2 μm); passivation layers over Al metallization in device structures subjected to subsequent high-temperature steps and so on. However, over the years there was no detailed information about low-stress BPSG film applications in production processes and devices.

Considering BPSG film PMD applications, one could realize that as-deposited film stress value is not that important due to the film flow processing used in the main device technologies. For instance, for two popular production processes designated above as Method 5 and Method 8, typical stress values for as-deposited BPSG films are in the range of (4.3+6.5)×10⁸ dyne×cm⁻² (tensile), but (4.0+6.0)×10⁸ dyne×cm⁻² (compressive), respectively. Post-deposition BPSG film anneal allowed eliminating stress differences due to the film flow.

18.6. BPSG FILM APPLICATION AS LOW-TEMPERATURE DIFFUSION SOURCE

CVD BPSG films can also serve as lower-temperature doped-oxide solid-to-solid diffusion sources [50]. For example, BPSG film with 4 wt % [B]–4 wt % [P] deposited on a 70 ohm-cm p-type wafer and subjected to a 60-min heat treatment at 900 °C, produced a 5-ohm/square n-type surface layer. Although the BPSG films are a source of both B and P atoms, the principal dopant in the silicon is P (because of relative differences in the distribution coefficients of the two dopants at the Si-SiO₂ interface). The principal effect of
the boron oxide in the glass is to lower the viscosity, thus permitting more phosphorus atoms to reach the Si/SiO₂ interface. A bare silicon wafer adjacent to BPSG in furnace will be boron-doped because of the relatively high volatility of boron oxide.

18.7. BPSG Film Application Peculiarities

As a final point of BPSG film application, it is necessary to mention that the gamma-ray hardness of BPSG films deposited by Method 1 at atmospheric pressure was reported to be much higher than that of PECVD from a hydride–nitrous oxide mixture, while the film compositions were the same [164]. The high radiation hardness of the former glass was explained due to a balance between electron and hole traps in the glass. The radiation susceptibility of the latter was attributed to phosphorus only, which was considered responsible for hole centers.

As noted in Part 1, weak oxidizing agents such as nitrous oxide are inadequate in terms of deposition kinetics. In addition to that, it is necessary to note that there were a few publications devoted to some issues with PECVD BPSG films deposited with the use of silane and nitrous oxide [256,288,290] according to Method 7 (see details in Chapter 6). Summarizing these observations, one can conclude that the most reasonable cause of differences of the properties of the BPSG films is non-complete oxidation of phosphorus and the formation of phosphorus species in P⁵⁺ and P⁰ state instead of P⁵⁺ state as per normal to form completely oxidized P₂O₅. However, it can be noted that Method 7 is used quite rarely.

18.8. Other BPSG Film Application Data

In [265], dielectric properties of BPSG films (named borophosphosilicate glass-ceramics) were evaluated. The films were synthesized by a sol-gel process using boric acid, phosphoric acid and tetraethoxyorthosilicate (TEOS) as starting compounds. The borophosphosilicate glass-ceramics was sintered below 950 °C in air. The structure of these glass-ceramics was studied by X-ray diffraction and SEM. It was found that the SiO₂ glass phase wraps up BPO₄ crystallites. S_i₃(PΟ₄)₃ crystallites exist when the SiO₂ content is decreased. The authors found that between 400 and 950 °C, the liquid faction of glass and the crystallization of crystal concurred to keep the chip in shape. The size of the BPO₄ crystalline grains was about 100 nm. The measurements for the dielectric properties of the sintered glass-ceramics show a dielectric constant of less than 5 and a dielectric loss factor of less than 3×10⁻³. It was concluded that this glass-ceramics showed a good potential for its use as dielectric materials in super high frequency multi-layer chip inductors.

The authors of [252,263] studied relaxation mechanisms of strained films bonded to oxide and low viscosity glass films. Relaxation of compressively strained heteroepitaxial Si₀.₇Ge₀.₃ films bonded to high and low viscosity glass compliant layers was investigated in [252]. These structures were formed by transferring Si₀.₇Ge₀.₃ films to Si substrates covered with thermal SiO₂ and BPSG films. Relaxation was studied through thermal annealing experiments. For the low viscosity BPSG, relaxation was observed near 800 °C and was accompanied by buckling of the Si₀.₇Ge₀.₃ film. At this temperature, no change in the
Si_{0.7}Ge_{0.3} film bonded to thermal SiO_2 was observed, and through this comparison relaxation on BPSG is interpreted as the result of viscous flow of the glass. Finally, film buckling was successfully avoided by patterning the strained films into small areas prior to annealing, and is an indication of film expansion. In [263], a process was recently developed to fabricate a structure comprising, from top to bottom, a SiGe thin film, a glass film, and a Si wafer. The SiGe film was patterned into islands. On annealing, the glass flowed and the islands relaxed. The resulting strain-free islands were used as substrates to grow epitaxial optoelectronic devices. The authors determined the conditions under which the islands relax by expansion without significant wrinkling, and demonstrate that a cap layer suppresses wrinkles, relaxing a large island crack-free.

The authors of [282] studied the stability of luminescent trivalent Cerium in silica host glasses modified by boron and phosphorus. Ce-doped BSG, phosphosilicate PSG, and BPSG films with different compositions were prepared by the sol-gel method, as silica films were used for comparison. The homogeneous rare-earth dispersion in the host matrix and the stabilization of the Ce^{3+} oxidation state enhanced the intensity of the photoluminescence emission in PSG and BPSG with respect to BSG and silica. The energy of the Ce^{3+} emission band in PSG and BPSG matrixes agreed with the phosphate environment of the rare earth.

**Final Remarks on Part 3**

Part 3 of the monograph describes different aspects of BPSG thin film implementation in electronic technologies. The main application of BPSG thin films in IC technologies is based on the film flow capability. This is necessary to smooth sharp edges of device structures and to eliminate voids in narrow IC device gaps covered with BPSG films. Analysis of BPSG film flow capability data has been performed quantitatively for traditional furnace thermal anneal, and Rapid Thermal Anneal. Detailed analysis of flow aspects of BPSG films has been presented using examples of the real IC device structures with steps and gaps. It is important to note that BPSG flow data were obtained experimentally using the scanning electron microscopy technique. It has been shown that the approaches presented can be applied to explain the flow of other types of flow-able glass films, for instance, BPSG films with a germanium oxide additive. Eventually, multi-factorial dependencies of the film flow capability have been presented. This summarized knowledge can be effectively used for time-consuming evaluation of the film flow on real IC device structures.

The quantitative BPSG flow description together with the quantitative moisture absorption and defect formation description made in Part 2 of the monograph, allowed the author to state simple quantitative approaches for obtaining the optimized BPSG composition used in electronic technology. These approaches and drawn formulas were proven using a number of experimental data, which showed good correlation.

Some rarely discussed aspects regarding the film durability have also been analyzed. Deep understanding on the causes of potential film instability and approaches to improve BPSG film post deposition thermal treatment have been proposed by the author for the first time.
Generalized data and equations presented in this chapter provide sufficient information for researchers and engineers regarding directions and details of BPSG film application in electronic-related technologies.