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DEPOSITION OF BOROPHOSPHOSILICATE GLASS FILMS USING THE TEOS–DIMETHYLPHOSPHITE–TRIMETHYLBORATE SYSTEM

Modernization of horizontal low pressure deposition system has been performed. The liquid source delivery system using the bubblers has been developed. The PSG and BPSG film deposition processes and film properties using TEOS-Dimethylphosphite-TEB system have been studied. It is shown that the use of dimethylphosphite allows varying the phosphorus concentration in the wide range. It is found that the optimal range of the total boron and phosphorus concentration ensuring the acceptable topology planarity and resistance to defect formation during storage is 8.7 ± 0.3 wt% when the phosphorus concentration is 3.0–3.8 wt%. It is found that at use of the TEOS-DMP-TEB system the depletion of the phosphorus concentration along reaction zone does not occur, and the total dopant concentration is practically constant. At the same time the deposition rate of BPSG films is 9.0–10.0 nm/min and the good film thickness uniformity are ensured. The as-deposited films have “mirror-like surface” that is proof of minimal surface roughness. The BPSG films with optimal composition are characterized by the reduced reaction capability against atmospheric moisture.

Keywords: borophosphatesilicate glass, deposition, topological relief planarity.

With shrinking device geometries the task of planarizing surface topography becomes more important [1]. Phosphosilicate glass (PSG) and borophosphosilicate glass (BPSG) are widely used for this purpose [2]. These binary and ternary glass films have an intrinsic flow property due to the temperature dependence of glass viscosity. BPSG films are also more attractive for use than PSG in contact reflow process (second thermal reflow), which is used for rounding of sharp contact edges to improve the step coverage by subsequent metal film. PSG and BPSG films are mostly produced by oxidation of silane [3] or pyrolytic decomposition of tetraethylorthosilicate [4, 5] with the addition of boron and phosphorus dopants during deposition.

The main disadvantages of silane-based processes are using toxic reagents, difficulty of process control, relatively high defect density of deposited films because the oxidation of silane (and phosphine) proceeds by the free-radical chain mechanism with intermediates being formed in the gas phase [6, 7]. Furthermore, silane processes take place at a relatively low temperature and cannot provide good step coverage. Silane based BPSG films need high doping to provide flowability, but this also leads to poor film stability in storage. Using organosilicon compounds (TEOS) allows to obtain the high-quality films [8], to reduce noxious emissions [9], and to improve step coverage

[10] and narrow gap filling [5, 11]. Nonetheless, moisture absorption and defect formation in highly doped glass films are still big challenges for these solutions.

Table 1 summarizes physical and chemical properties of common source materials for the deposition of PSG and BPSG films. With the TEOS–trimethylphosphate(TMPO)–O₂ and TEOS–TMPO–trimethylborate(TMB)–O₂ systems, films of over 3 wt% P are relatively difficult to produce because TMPO has a low vapor pressure [13, 14]. Furthermore, the P concentration of BPSG films is known to be strongly dependent on the temperature of deposition when this involves TMPO [15].

Fig. 1 depicts the dependence of the B and P concentrations in BPSG films on the deposition temperature in the case of the TEOS–trimethylphosphite(TMPite)–TMB–O₂ system. Notice that the P concentration falls from 4.2 to 1 wt% at a rate of about 0.06 wt%/deg as the deposition temperature is raised from 675 to 725°C, while the B concentration remains fairly constant at 6.2–6.4 wt%. The authors of [13] have shown that a flow angle α less than 45° is achieved when the sum of the B and P concentrations exceeds 8.7 wt%, provided that they are greater than 5.65 and 1.4 wt%, respectively. On the other hand, boron-rich films are very hygroscopic and unstable in storage [16–19] and are not adequate in gettering alkali

Table 1
Physical and chemical properties of common source materials for the deposition of PSG and BPSG films

Material	Abbreviation	Chemical formula	Relative molecular mass	Physical state	Melting point, °C	Boiling point, °C	Density, g/cm ³ (gas), g/ml (liquid)	Refractive index	Threshold limit value, mg/m ³
Monosilane	—	SiH ₄	32.12	gas	-185	-112	1.44	—	1.0
Tetraethylorthosilicate	TEOS	(C ₂ H ₅ O) ₄ Si	208.34	liquid	-82.5	166.5	0.968 ^{25°C}	1.3837	20
Dimethyldichloro-silane	DMDCS	(CH ₃) ₂ Cl ₂ Si	129.06	liquid	-36	70.3	1.064 ^{20°C}	1.4055	1.0
Phosphine	—	PH ₃	34.0	gas	-133.8	-87.4	1.53	—	0.1
Trimethylphosphate	TMP, TMPO	(CH ₃ O) ₃ PO	140.07	liquid	-46	193–197	1.214 ^{25°C}	1.4089	2.69
Trimethylphosphite	TMPite	(CH ₃ O) ₃ P	124	liquid	-78	111	1.052	—	—
Dimethylphosphite [12]	DMP	(CH ₃ O) ₂ P(O)H	110.04	liquid	—	170.5	1.1944	1.4036	—
Phosphorus trichloride	—	PCl ₃	137.33	liquid	-90.3	75.1	1.557	1.516	0.2
Phosphorus oxychloride	—	POCl ₃	153.33	liquid	—	105.8	1.675	1.460	0.05
Diborane	—	B ₂ H ₆	27.67	gas	-165.5	-92.5	1.24	—	0.1
Trimethylborate	TMB	(CH ₃ O) ₃ B	103.91	liquid	-34	68-69	0.915 ^{20°C}	—	—
Triethylborate	TEB	(C ₂ H ₅ O) ₃ B	145.99	liquid	-84.5	117.4	0.858	—	—
Tripentylborate	TPB	(C ₃ H ₇ O) ₃ B	188.08	liquid	—	175–178	0.86 ^{25°C}	1.394	—
Boron trichloride	—	BCl ₃	117.17	liquid	-107	12.4	1.434	1.428	—

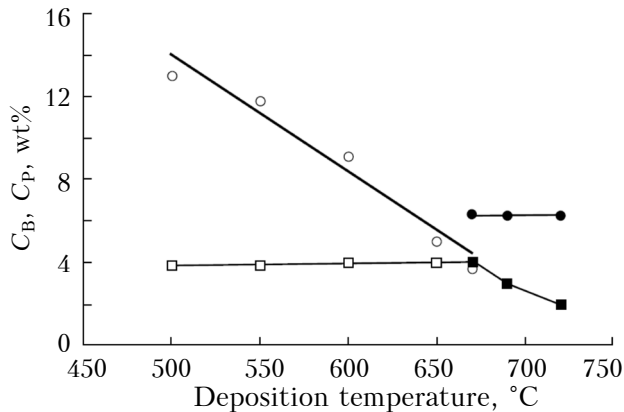


Fig. 1. Previously reported boron (C_B) and phosphorus (C_P) concentrations in BPSG films vs. deposition temperature in the case of the TEOS–TMPite–TMB– O_2 system
 □ – boron [13]; ● – boron [15]; ○ – phosphorus [13];
 ■ – phosphorus [15]

metals (ions). Moreover, using the boron-rich BPSG films can cause the contact-to-contact short failure in ultra large-scale integration by wiggling contact profile [20].

Furthermore, with the TEOS–TMPO–TMB system, the considerable depletion of phosphorus

along the deposition zone makes it difficult to strike a balance between the deposition rate, the amount and the uniformity of P concentration, and the thickness uniformity.

In view of the above, we find it worthwhile to identify alternative systems of source materials for the deposition of PSG and BPSG films that would allow a higher degree of control over the B and P concentrations and better thickness reproducibility in deposition, and would provide films more stable in storage. The TEOS–DMP, TEOS–DMP–TEB, and TEOS–DMP–TMB systems are of particular interest in these respects. This paper presents an experimental investigation into the deposition kinetics of PSG and BPSG films from the TEOS–DMP–TEB(TMB) reactant system, and into the properties of the films.

Experiment

The experiments were performed using 4 inch B-doped, <100> oriented, 12 Ω -cm resistivity silicon wafers as substrates.

The deposition of PSG and BPSG films was carried out in a horizontal hot wall LPCVD reactor (Karat model) [18], using liquid reagents. Since the liquid reagents have different saturated-vapor pressure at the same temperature, the separate bubbling evaporators were used for each liquid

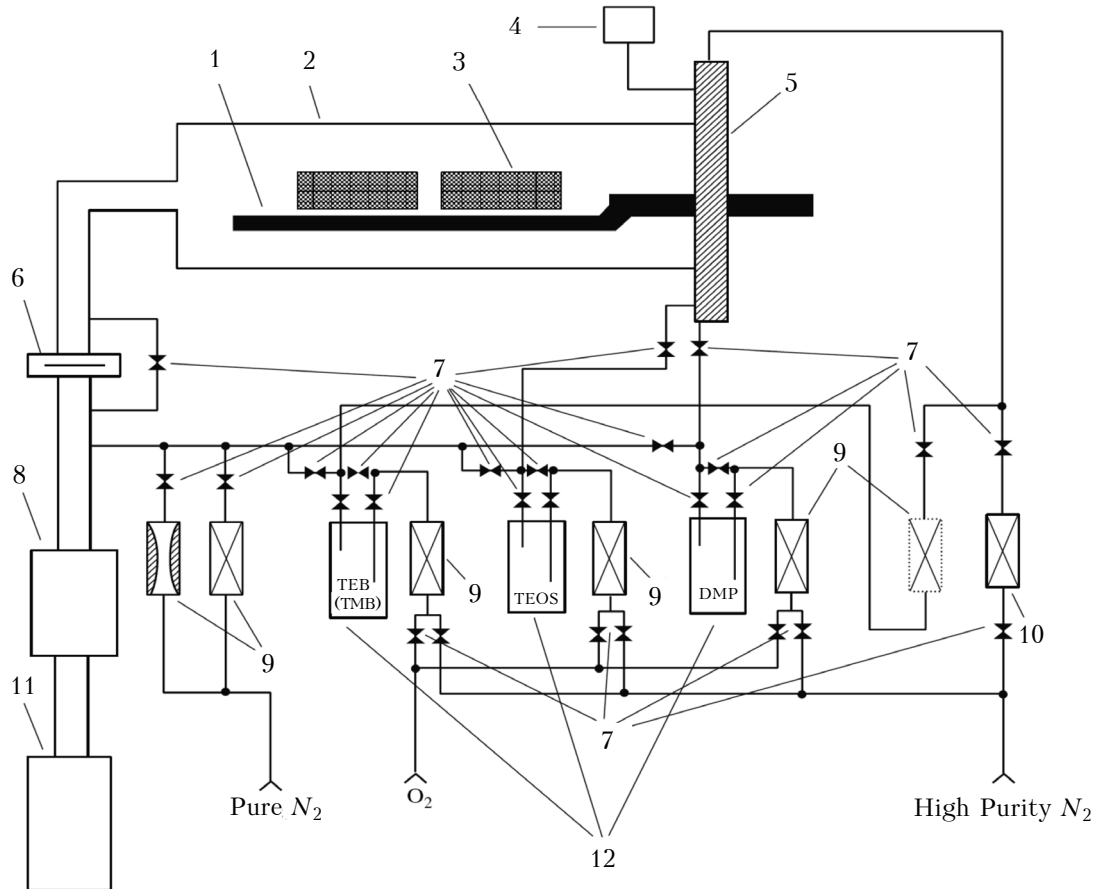


Fig. 2. Gas and vapor distribution system of the LPCVD reactor:

1 – SiC cantilever; 2 – quartz reactor; 3 – wafer boat; 4 – pressure gauge; 5 – shutter; 6 – vacuum gate; 7 – valves; 8 – nitrogen trap; 9 – mass flow controllers; 10 – valve with calibrated orifice for nitrogen backfill; 11 – vacuum pumps; 12 – TEB (TMB), TEOS, DMP bubblers (the TEOS and DMP bubblers use the carrier gas)

reagent. The gas and vapor distribution system is presented in Fig. 2.

The special liquid vaporizing system was used to provide the stable pressure and flow of TEOS vapor. This system contains the bulk supply container (10 liters), compartment with metallic container (bubbler) for holding TEOS to be vaporized, mass flow controller (MFC) for carrier gas and a bubbling tube inserted into bubbler, an outlet pipe for ejecting TEOS vapor with carrier gas, liquid supply pipe for refilling the bubbler from bulk container, temperature detection and adjustment means for maintaining the TEOS temperature and temperature inside the bubbler compartment. This liquid vaporizing system can be operated under temperatures above 50°C, which are needed for TEOS evaporation in case of BPSG deposition in horizontal LPCVD reactor. The TEOS vapor pipes to reactor were electrically heated 5–10°C above the temperature of the bubbler, using insulated wire.

The liquid source materials were TEOS (distilled), dimethylphosphite, and trimethylborate conforming to the Russian technical specifications TY 2637-059-44493179-04, TY 2634-002-40475629-99, and TY 2634-001-40475629-99, respectively. They were evaporated in the respective temperature ranges 55–57, 22–24, and 20–40°C, with each temperature point maintained to within $\pm 0.5^\circ\text{C}$. The wafers were placed in specially designed perforated quartz boats. The wafer spacing was 7.5 mm.

The PSG films were deposited at 680–715°C and 45 $\pm$ 3 Pa; the BPSG films – at 660–690°C and 45 $\pm$ 3 Pa. The chamber pressure was maintained by feeding nitrogen through MFC. The carrier gas was oxygen or nitrogen; its flow rate through each bubbler was 200 sccm or less.

The PSG and BPSG deposition process included the following steps:

1. Loading wafers into the chamber and nitrogen purge through the chamber;
2. Chamber pumpdown;
3. Nitrogen purge of the chamber;
4. Chamber pumpdown, temperature stabilization at given values;
5. Leak check;
6. Chamber pumpdown;
7. Deposition of BPSG films;
8. Nitrogen purge of the chamber and chamber pumpdown;
9. Repeat step 8 an appropriate number of times;
10. Chamber backfill using nitrogen until atmospheric pressure is reached;
11. Unloading wafers.

Film thickness was measured by spectrophotometry (Leica's MPV-SP), the phosphorus concentration by X-ray fluorescence (Rigaku's M3613), the boron concentration by infrared (IR) spectroscopy (SPECORD-75) and Fourier-transform spectroscopy (FSM-1201 FTIR analyzer), and refractive index by laser ellipsometry (LEF-3M).

The test structure, having the polysilicon lines 1 μm thick was used for evaluating topology planarity. The films 0.75 $\pm$ 0.05 μm thick were subjected to thermal reflow in dry oxygen at 850°C during 45 min for BPSG or at 950°C during 30 min for PSG. The topology planarity was evaluated by measuring the slope angle α after reflow [4, 8] as seen in cross-sectional scanning-electron-microscope images.

Results and discussion

Fig. 3 and 4 depict the observed dependence of P concentration in PSG films on deposition temperature and DMP temperature, respectively, with the carrier gas flow rate maintained at 200 sccm. The P concentration decreases steadily from 10.0 to 6.0 wt% as the deposition temperature is elevated from 680 to 715°C when DMP temperature is about 30°C (Fig. 3). It also increases steadily with DMP temperature (Fig. 4).

When nitrogen is used as the carrier gas, increasing its flow rate from 67 to 200 sccm reduces the PSG deposition rate from 7.5 to 5.5 nm/min, that can be explained by the TEOS partial pressure reduction. The carrier-gas flow rate has a significant influence on the wafer-to-wafer (w/w) thickness uniformity: raising the former to 200 sccm

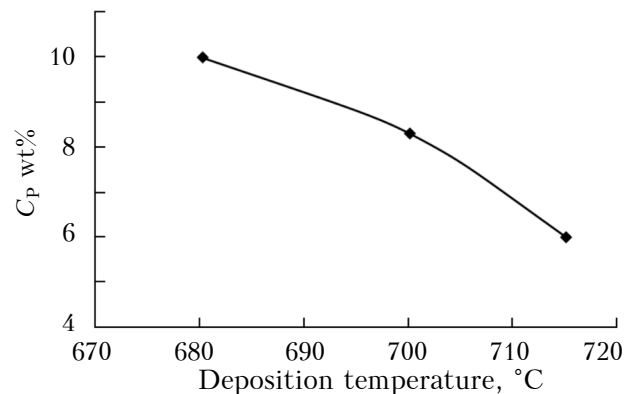


Fig. 3. Phosphorus concentration vs. deposition temperature for PSG films

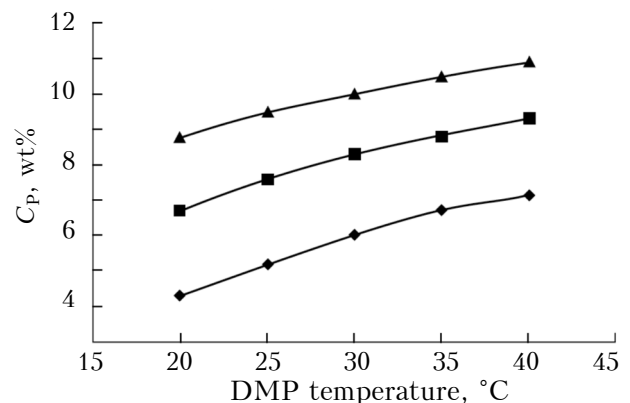


Fig. 4. Phosphorus concentration vs. DMP temperature for PSG films at a deposition temperature of 715 (◆), 700 (■) and 680 °C (▲)

improves the w/w thickness uniformity from ± 12.6 to $\pm 4.6\%$. Using oxygen as the carrier gas increases the deposition rate by a factor of 1.3 and provides an increase in average P concentration by about 1.5 wt%. Those might be related to the increase in the number of P–O bonds in the film being deposited. The within wafer thickness uniformity of PSG films was less than $\pm 5.0\%$ for each of the processes performed. The PSG films have a refractive index of 1.45 ± 0.01 .

The dependences of phosphorus concentration on the deposition temperatures and DMP bubbler temperature makes enable to control the concentration of phosphorus over wide ranges.

The process temperature is known to be a major factor in BPSG deposition using the TEOS–TMPO–TMB system [21, 22]. It has been found experimentally that phosphorus plays the central

role because its excess or deficiency accelerates or inhibits the deposition process, respectively. Note also that it is very difficult to provide an adequate thickness uniformity when the deposition process is carried out at $590–680^\circ\text{C}$, on the other hand, lower temperatures result in a sharp decrease in deposition rate. Therefore, the determination of optimal BPSG deposition conditions should be based on a compromise between individual process parameters.

Using the TEOS–DMP–TEB(TMB) system, we have obtained stable BPSG films with $C_P + C_B = 8.5–9.3$ wt% and $C_B = 3.4–4.7$ wt% (see **Table 2**). Acceptable slope angles after reflow have been achieved at $C_P + C_B = 8.7–9.2$ wt% and $C_P = 2.4–5.0$ wt% (see **Table 3**). It was defined that the formation of boric acid crystals in 8 hours after deposition when boron concentration

was more than 6.3 wt%. With phosphorus concentration over 5 wt% the defect formation after thermal treatment was observed. The side wall step coverage by BPSG films was 0.56 at 320°C , 0.73 at 430°C and 0.87 at 650°C [9], which are in good agreement with experimental results of other authors [23, 24].

Table 4 lists major process characteristics and compares them with those reported previously. Since the BPSG deposition rate is very sensitive to the DMP flow rate, it is advantageous to maintain C_P between 3.0 and 3.8 wt% to provide the stability and reproducibility of film thickness uniformity. Such BPSG films are deposited at $9.0–10.0$ nm/min and have a refractive index of $1.45–1.46$.

When DMP is used as a phosphorus source, the C_P profile is virtually independent on the deposition temperature profile. The TEOS, DMP, and TEB flow rates – and therefore C_B and C_P – are mostly determined by the bubbler temperatures. For the first time, it was found that there is no depletion in phosphorus

BPSG film stability

Table 2

Process no.	C_P , wt %	C_B , wt %	$C_P + C_B$, wt %	Defect formation in X hours after deposition				
				0,3 h	2 h	4 h	24 h	72 h
1	4.8	7.5	12.3	+	+	+	+	+
2	2.7	6.9	9.6	–	+	+	+	+
3	6.2	4.4	10.9	–	+	+	+	+
4	1.2	7.0	8.2	–	–	+	+	+
5	1.7	6.9	8.6	–	–	+	+	+
6	6.5	3.7	10.2	–	–	+	+	+
7	7.0	3.5	10.5	–	–	+	+	+
8	7.1	3.2	10.3	–	–	+	+	+
9	1.6	6.6	8.2	–	–	–	+	+
10	2.4	6.4	8.8	–	–	–	+	+
11	3.2	6.0	9.2	–	–	–	+	+
12	5.1	4.5	9.6	–	–	–	+	+
13	5.6	4.2	9.8	–	–	–	+	+
14	6.1	3.6	9.7	–	–	–	+	+
15	7.4	2.5	9.9	–	–	–	+	+
16	3.0	5.8	8.8	–	–	–	–	+
17	3.9	5.0	8.9	–	–	–	–	+
18	4.7	4.9	9.6	–	–	–	–	+
19	5.0	4.1	9.1	–	–	–	–	+
20	4.2	4.7	8.9	–	–	–	–	–
21	4.8	3.8	8.6	–	–	–	–	–
22	5.1	3.4	8.5	–	–	–	–	–
23	5.9	3.4	9.3	–	–	–	–	–

Note: The plus and minus signs indicate the presence and absence of defects, respectively.

Slope angle α after BPSG reflow as dependent on film properties and process parameters

Table 3

Wafer no.	Film thickness, μm	C_P , wt%	C_B , wt%	$C_P + C_B$, wt%	α , deg	Deposition rate, nm/min	Thickness uniformity within wafer, $\pm\%$
1	0.75	2.4	6.4	8.8	39	7.0	4.2–6.0
2	0.73	5.0	4.1	9.1	31	11.9	5.0–6.8
3	0.76	2.8	5.9	8.7	35	7.9	3.4–4.2
4	0.60	1.2	7.0	8.2	61	4.8	2.1–2.7
5	0.75	6.1	3.6	9.7	46	14.7	3.9–5.6
6	0.74	4.6	4.5	9.1	30	11.6	2.4–5.3
7	0.39	3.2	6.0	9.2	39	8.9	2.8–4.6

Table 4

Major characteristics of BPSG deposition process as compared with previous results

Reagents	Through-put, wafers/batch	Wafer diameter, mm	Pressure, Pa	Temperature, °C	Deposition rate, nm/min	C_P , wt %	C_B , wt %	Thickness uniformity within wafer, $\pm\%$	Dopant range, w/w, $\pm$ wt %
TEOS, PH_3 , O_2 , TMPO, TMPite [4]	90	100	66.5	620–680	15	10.8	5.6	4.0	1.5
TEOS, TMB, TMPite, O_2 , N_2 [4]	50	60	40–106	675–750	10–30	4.0	4.0	—	—
DMDCS, phosphorus chlorides, ethyl borates, O_2 , N_2 [4]	50	100	200	750–850	8–13	9.7	9.5	5.0	—
TEOS, TMB, TMPite, O_2 , N_2 [4]	30	100	40	510–680	5–15	5.0	13	10.0	—
DADBS*, TMB, TMPite [4]	50	60	66.5	470–550	2–25	4.0	5	—	—
TEOS, DMP, TEB (TMB) [present work]	50	150	45	660–690	9.0–10.0	3.0 ... 3.5	5.0 ... 5.5	4.8	0.4

* DADBS — di-acetoxy-di-t-butoxy-silane.

concentration along the deposition zone when the TEOS–DMP–TEB system is employed; and C_B+C_P is almost uniform.

As-deposited films have mirror-like surface and roughness of 0.3–0.35 nm, which is three times lower than that for BPSG films in [23] and 2.7–3.6 lower than for PSG films, obtained using TEOS-DMP (0.97–1.09 nm).

BPSG films have density of 2.22 g/cm³ at 320–430°C and 2.30 g/cm³ at 650°C, respectively [10]. Note that BPSG flowability is more sensitive

to boron than to phosphorus; for example, reducing α from 30° to 20° requires 1 wt% increase in C_B or 7 wt% increase in C_P [21].

Fig. 5 depicts a correlation between moisture absorption and dopant concentrations for BPSG films, which were defect-free in 24 hours after the deposition (H — moisture penetration depth). Previously, stable BPSG films were produced with deposition followed up by in-situ thermal reflow. This was necessary because the range of optimum boron and phosphorus concentrations was above

the defect formation boundary, as seen in Fig. 5. In another study, 24-h stability of BPSG films was achieved within narrow ranges of C_B and C_P [26]. Using the TEOS–DMP–TEB system, we were able to expand dopant concentration ranges because DMP allows obtaining higher phosphorus concentration under higher deposition temperatures; furthermore, the range of optimum boron and phosphorus concentrations is below the defect formation boundary (Fig. 5).

In situ thermal reflow [13] was also employed in the present study and it as well allowed to obtain BPSG films that were immune to defect formation in the subsequent process steps and during storage, and to considerably reduce the defect density by eliminating exposure of as-deposited films to the air.

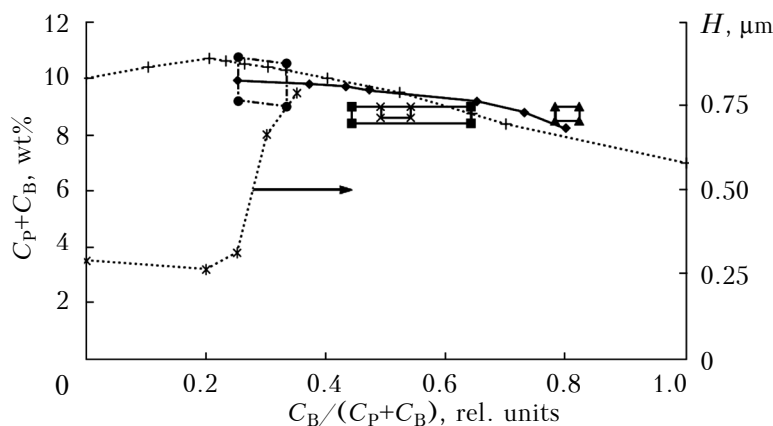


Fig. 5. Correlation between the moisture absorption and dopant concentrations of BPSG films [13]:

◆ — defect formation boundary [this work]; ▲ — TEOS–DMP [this work]; ■ — TEOS–TMPate [13]; × — APCVD BPSG [26]; * — moisture penetration depth [28]; ● — optimum region [25]; + — defect formation boundary [25]

Table 5

The comparison of deposition process parameters and properties of BPSG films, obtained on different types of tool [27]

Parameter	Tool model		
	Horizontal LPCVD system "Karat"	Concept-1 (Novellus)	Precision-5000 (Applied Materials)
Process type	Low pressure CVD	Plasma enhanced CVD	Plasma enhanced CVD
Reactor type	Batch (Furnace)	Single wafer (multiposition)	Single wafer
Temperature	700°C	400°C	39°C
Silicon source	TEOS	SiH ₄	TEOS
Phosphorus and boron source	DMP, TMB	PH ₃ , B ₂ H ₆	TMPO, TMB
Deposition rate, nm/min	9.4	700	760
Within wafer thickness uniformity (6 inch), %	≤±5.0	≤±1.5	≤±2.0
Refractive index	1.46±0.01	1.46±0.01	1.46±0.01
Density, g/cm ³	2.28–2.3	2.12–2.18	2.12–2.27
Range of optimal dopant concentration, wt%, and time to defect formation, h	P: 3.0–4.0 B: 6.0–5.0 >>24	P: 4.0–4.5 B: 4.5–4.0 >24	P: 3.0–3.5 B: 5.5–5.0 >24
Total dopant concentration, wt%	8.5–9.0	8.0–8.5	8,0–8.5
Throughput, w/h	12–15	20	20 (2 chamber)

Note: Boron and phosphorus concentration uniformity are ±0.5 и ±0.2 wt%, respectively.

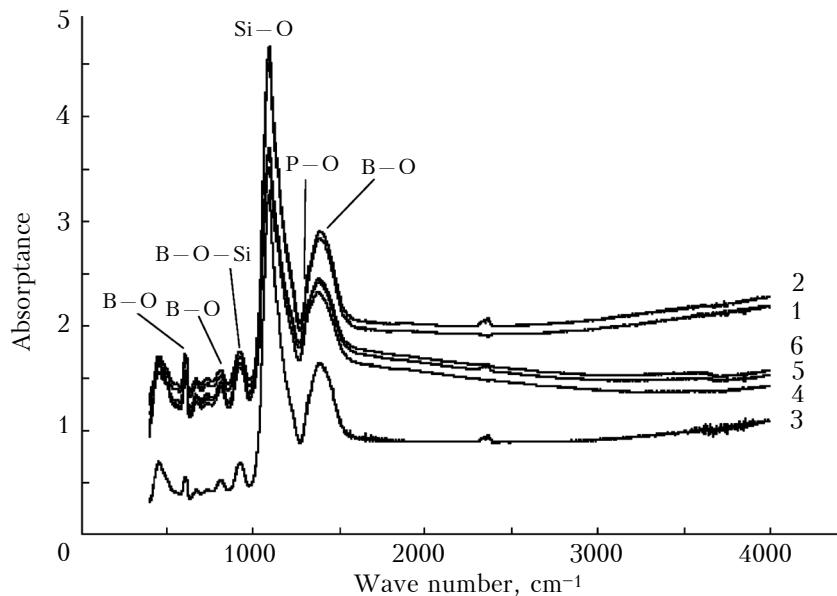


Fig. 6. IR absorption spectra of BPSG films measured immediately after deposition (1, 4), 12 days (2, 5) and 30 days (3, 6) after deposition, and of films subjected to in-situ thermal reflow (4–6)

Table 5 lists the comparison of deposition process parameters and properties of BPSG films, obtained on different types of tool [27].

Fig. 6 presents the IR absorption spectra of BPSG films some of which were subjected to in situ thermal reflow, the spectra being measured immediately, 12 days, and 30 days after deposition. It is seen that the spectra of as-deposited films, whether or not thermal reflow has been applied, do not exhibit dips or oscillations in the wave-number ranges 2900–3640 and 1500–1600 cm⁻¹,

indicating zero water content. During 12 days of storage, BO–H bonds are formed in unreflowed films, as evidenced by weak peaks near 2250 cm⁻¹ and oscillations in the ranges 2900–4000 and 1500–1600 cm⁻¹ [28]. The spectra of reflowed films do not have such peaks and show small oscillations over the wave numbers 1500 to 1600 cm⁻¹. Dips in the range 3500–3800 cm⁻¹ start to appear after the 14th day of storage. Thus, the IR spectroscopy data provide evidence that the BPSG deposition method used in this study

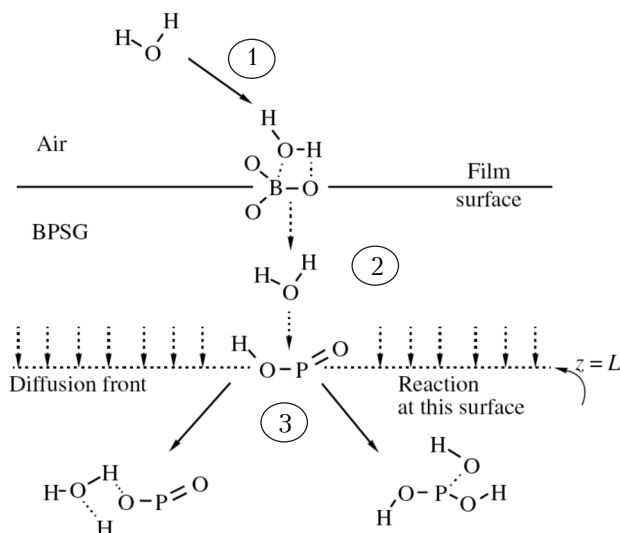


Fig. 7. Mechanism of glass-water interaction in a BPSG film:

1 – water adsorption at B–O surface centers; 2 – bulk and surface diffusion of water molecules toward P centers; 3 – reaction with P–O or the formation of a hydrogen bond with P–O

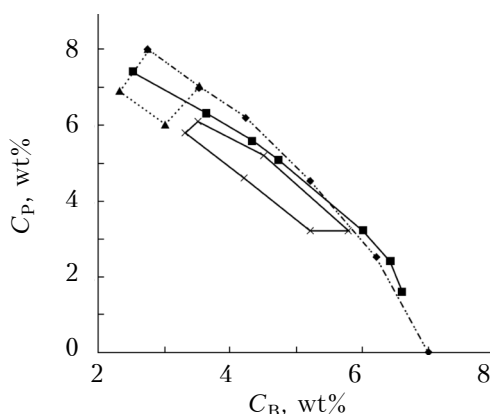


Fig. 8. Ranges of optimum B and P concentrations in BPSG films identified in this study and earlier from the viewpoint of structural quality and planarity:

◆ – defect limit [29]; ■ – defect limit [this study]; ▲ – optimum range [29]; × – optimum range [this study]

research allows to obtain films of low porosity and sufficiently high density, which absorb less moisture in storage.

In porous BPSG films, moisture absorption is assumed to proceed through pores. For dense, reasonably ordered films, the mechanism is more complicated; it is illustrated in Fig. 7 [28]. Water molecules are first adsorbed by B–O bonds. Then adsorbed water molecules diffuse inward and react with P–O groups, forming P=O and PO=H bonds; the reaction with P=O constitutes the rate-determining step of adsorption. However, if the porosity is high enough, diffusion proceeds much faster than this reaction, resulting in a linear dependence of moisture penetration depth on storage time; that is typical for boron-rich BPSG

films. Indeed, BPSG films deposited using the TEOS–DMP–TEB system are characterized by a smaller moisture penetration depth as compared with films obtained by hydride oxidation. The defect formation boundary for such BPSG films moves to higher B concentrations (Fig. 5). Thus, obtained BPSG films are less reactive with moisture and have a high density. These are characteristic features of type II films, which have a dense structure and homogenous distribution of boron and phosphorus oxides [29].

Fig. 8 compares the regions of optimal dopant concentrations in BPSG films identified in this study and earlier from the viewpoint of film stability and planarity after reflow. Note also that TEB can be replaced with TMB, a less expensive reagent, without compromising the structural stability, moisture resistance, and other important properties of films. Having a higher vapor pressure, TMB requires no bubbling, provides a more uniform boron concentration along the deposition zone, and is consumed in smaller quantities.

The combined process of BPSG deposition and in-situ thermal reflow is protected by patent [30], as well as the PSG deposition process using the TEOS–DMP system [31, 32] and the BPSG deposition process using the TEOS–DMP–TEB (TMB) system [33, 34].

Conclusions

The authors investigated the chemical vapor deposition of PSG and BPSG films from the TEOS–DMP–TEB(TMB) reactant system at 660–715°C in horizontal LPCVD reactor equipped with a specifically designed system for supplying each liquid reagent to reactor. The special liquid vaporizing system was used to provide the stable pressure and flow of TEOS vapor.

The authors found that using the DMP allows varying the concentration of phosphorus in PSG films over wide ranges. We identified the optimal range of the total boron and phosphorus concentration ensuring the acceptable topology planarity and resistance to defect formation during storage that is 8.7–0.3 wt% when the phosphorus concentration is 3.0–3.8 wt%. The defect formation boundary for such BPSG films moves to higher B concentrations. We found that at use of the TEOS–DMP–TEB system the depletion of the phosphorus concentration along reaction zone does not occur, and the total dopant concentration is practically constant. The developed process has the deposition rate of 9.0–10.0 nm/min and ensures the good film thickness uniformity and the reduced reaction capability of BPSG films against atmospheric moisture. The side wall step coverage by BPSG films was 0.56 at 320°C, 0.73 at 430°C and 0.87 at 690°C. As-deposited films have mirror-like surface and roughness of 0.3–0.35 nm, that is 2.7–3.6 times lower than for PSG films, obtained using TEOS–DMP (0.97–1.09 nm).

In situ thermal reflow was also employed in the present study and it as well allowed to obtain BPSG films that were immune to defect forma-

tion in the subsequent process steps and during storage, and to considerably reduce the defect density by eliminating exposure of as-deposited films to the air.

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ОСАЖДЕНИЕ ПЛЕНОК БОРОФОСФОРОСИЛИКАТНОГО СТЕКЛА С ИСПОЛЬЗОВАНИЕМ СИСТЕМЫ ТЭОС-ДИМЕТИЛФОСФИТ-ТРИМЕТИЛБОРАТ

Проведена модернизация горизонтального реактора пониженного давления. Разработана система подачи жидкого реагента с использованием барботеров. Исследованы процессы осаждения пленок и свойства пленок ФСС и БФСС с использованием системы ТЭОС-диметилфосфит(ДМФ)-триметилборат(ТМФ).

Ключевые слова: борофосфоросиликатное стекло, осаждение, планарность топологического рельефа.

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ОСАДЖЕННЯ ПЛІВОК БОРОФОСФОРОСІЛІКАТНОГО СКЛА З ВИКОРИСТАННЯМ СИСТЕМИ ТЕОС-ДІМЕТИЛФОСФІТ-ТРИМЕТИЛБОРАТ

Проведено модернізацію горизонтального реактора зниженого тиску. Розроблено систему подачі рідкого реагенту з використанням барботерів. Досліджено процеси осадження плівок і властивості плівок ФСС і БФСС з використанням системи ТЕОС-діметилфосфіт(ДМФ)-тріметилборат(ТМФ).

Показано, що використання діметилфосфіта дозволяє варіювати концентрацію фосфору в широкому діапазоні. Встановлено, що оптимальний діапазон сумарних концентрацій бору та фосфору, що забезпечує прийнятну планарність топологічного рельєфу і стійкість до дефектоутворення при зберіганні, складає 8.7–0.3 ваг.%, При цьому концентрація фосфору становить 3.0–3.8 ваг.%. Встановлено, що при використанні системи ТЕОС–ДМФ–ТМБ не відбувається збіднення концентрації фосфору уздовж реакційної зони, а сумарна концентрація легуючих домішок залишається практично постійною. У той самий час забезпечуються швидкість осадження плівок БФСС 9.0–10.0 нм/хв та хороша однорідність товщини плівок. Свіжоосажені плівки мають «дзеркальну поверхню», що підтверджує їх мінімальну шорсткість. Плівки БФСС оптимального складу характеризуються зниженою реакційною здатністю по відношенню до атмосферної вологості.

Ключові слова: борофосфоросілікатне скло, осадження, планарність топологічного рельєфу.