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# MOLECULAR ENGINEERING IN SEMICONDUCTOR TECHNOLOGY : BOROSILICATEGLASS BY DECOMPOSITION OF A MONOMOLECULAR PRECURSOR

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**Résumé**

Des verres borosilicatés (BSG) ont été déposés CVD sous basse pression à parois chaudes, et CVD assiblé par plasma à parlis de Tris(trimethylsiloxy)boron = TTMSB = $B[OSi(CH_3)_3]_3$). Sous basse pression à 800 °C on obtient des verres à 4.7 % poids de bore. Par activation plasma il est possible de casser des liaisons déterminées dans la molécule initiale et de dêposer des films de haute qualité à 360 °C. Dans ce cas la teneur à bore peut varier de 0 à 5 % poids en changeant le paramêtres du procédé activé.

**Abstract**

Borosilicateglass (BSG) was deposited in a standard LPCVD-hotwall reactor and in a single-wafer PECVD-system using (Tris(trimethylsiloxy)boron = TTMSB = $B[OSi(CH_3)_3]_3$) as source material. The LPCVD-deposition of BSG at 800 °C yields films of about 4.7 wt% boron. It is possible by means of plasma enhanced CVD to crack definite bondings in the precursor molecule and to deposite high quality BSG-films while reducing the deposition temperature down to 360 °C. A further advantage of the PECVD-process is that the boron content in the layers can be varyied in the range of 0 - 5 wt% by changing the process parameters.

## Introduction

The basic idea of "molecular engineering" in semiconductor technology is to "program" the stucture and composition of thin layers like e.g. doped oxides as BSG by the source-material. Tailored molecules decompose into fragments containing a substructure of the layers to be built up. The deposition of borosilicateglass (BSG) by low pressure decomposition of the monomolecular precursor TTMSB at a temperature of 800 °C has successfuly shown that it is possible to yield films with inherently constant composition (e.g. a boron weight fraction of about 4.7 wt%) / Lit. 1 /. In order to reduce the deposition temperature plasma enhanced decomposition of molecules like TTMSB was studied hence not any clear understanding of the influence of growth parameters is reported.

## Technical Background

Highly integrated circuits like the 4M DRAM or the 16M DRAM (DRAM = dynamic random access memory) are realized using the technology of socalled trench-cells (capacitor-cells) with high aspect-ratios a (a = ratio of celldepth to diameter) / Lit. 2,3,4,5,6,7,8 /.

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The use of these trenches leads to a gain of area and thus in higher integration density if it is possible to place the trench-cells with minimal spacing apart from each other. This can be realized if the $n^+$-electrodes surrounding the trench-walls are separated by a $p^+$-doping between them. The realization of shallow junctions in bipolar technology requires well-known doping techniques too. Although the principal viability of several approaches has been established, a careful evaluation shows that only a minor fraction leads to production orientated processes.

A well-known method of doping silicon has been and still is ion-implantation. Ion-implantation might damage the silicon lattice or suffers from geometrical restrictions like e.g. shadowing effects resulting in a non-uniform distribution of the dopant. A further disadvantage is the low throughput.
Doping silicon by solid state diffusion using borosilicateglass present some advantages compared to standard technology. In production the "state of the art" has been films based on silane chemistry. The great advantage of these deposition procedures at atmospheric pressure is the relatively low deposition temperature of about 450 °C. Furtheron the silane chemistry is well understood. Despite these advantages silane-based deposition processes show up some disadvantages :

- The media used ($SiH_4$ and e.g. $B_2H_6$) are explosive and extremely poisonous.
- The processes are connected with high particle counts.
- The undensified films are not stable in environmental air.
- The dopant uniformity in the layers is inhomogeneous.
- The films show bad step coverage and poor dopant efficiency.

The use of organic liquids as precursors has solved a couple of problems . E.g. BSG-films produced with TEOS (Tetraethylorthosilicate) and TMB (Trimethylborate) have superior qualities in comparison to "silane-films" like excellent step coverage and good dopant efficiency. The precursors are normally non explosive and non corrossive media. The processes are less sensitive to moisture.

But the gain in process reliability is still connected with some disadvantages :

- The undensified layers are still instable in environmental atmosphere.
- There can be a pile-up of dopant elements in the silicon.
  The boron replaces either silicon or oxygen sites in the source layer matrix $SiO_2$. If boron replaces oxygen, the dopant becomes more and more immobile and during the drive-in an oversaturation occurs near the BSG/silicon interface which causes the socalled pile-up.
- The necessity to control two liquids with different vapor pressures rises complications in production process. Especially the complexity of the CVD-setups and the difficulties in performing the deposition process increase.
- The deposition temperature rises beyond the decomposition temperature of TEOS (> 700 °C).

The main interests concerning film properties in semiconductor technology are :

1. Well characterized structure (e.g. composition, lattice parameters)
2. Microstructure (e.g. pinholes, grain size, surface roughness)
3. Electrical active defects (e.g. traps)
4. Good step coverage
5. Stability under atmospheric environment
6. Uniformity in dopant distribution and film thickness
7. Lower deposition temperatures
8. Broad "process windows" (e.g. reproducibility)

This has led us to the objective of using molecules as precursors that already consist of the elements of the layer to be deposited and where the structure of the layers is partially preformed in the precursor molecule. Furthermore there should be only one liquid source to be controlled (temperature, gas flow etc.). To our knowledge, no consequent attempt has been made so far, to extend this principle to e.g. doped glasses used in semiconductor technology.

As an example for the successful implementation of "molecular engineering" into the fabrication of semiconductor devices a novel borosilicateglass deposition process is described either by thermal decomposition of TTMSB / **Lit.** 1 / or by means of plasma enhanced CVD (PECVD) at reduced deposition temperatures. The autors report a new way of prparing borosilicateglass starting from an elementorganic boron precursor. Although pertinent parameters are presented not any clear understanding of the influence of growth parameters is reported.

## Experimental

1. LPCVD-process :

The runs were carried out in a conventional LPCVD-setup (hotwall reactor) described before / **Lit. 14** / with TTMSB as source material. An optimum working point was at 800 °C, 100 Pa deposition pressure, 260 sccm $O_2$-flow and a bubbler temperature between 25 °C and 35 °C. Under these conditions a constant boron concentration in BSG of 4.7 wt% can be achieved. In addition to earlier experiments the main interest of the present work has been in influencing the boron weight fraction in the BSG-layers as a function of the process parameters like pressure, temperature oxygen flow.

2. PECVD-process :

The runs were carried out in a PECVD-setup (see **fig.** 1) by means of a statistical experimental design in order to minimize the amount of experiments. The main process parameters were RF-power, oxygen flow, carrier gas flow, susceptor temperature, process pressure and spacing of the electrodes. The layers have been characterized regarding deposition rate, thickness uniformity, boron content, stoichiometry and the carbon contamination. Some estimations have been done to get a feeling for the amount of plasma energy needed to influence the breaking of definite bondings in the molecule. IR-measurements gave us some additional hints to understand the glass formation process and the collapse of the precursor molecule used.

## Results

1. LPCVD-process :

**Figure** 2 describes the influence of deposition temperature on the boron weight fraction in the BSG-layers. The boron content shows a slight decrease with higher deposition temperatures.

**Figure** 3 describes the influence of the oxygen flow on the boron weight fraction of the samples. Additional oxygen clearly enhances the film growth. At higher oxygen flow this effect levels off. The intermediate maximum of thickness variation / **Lit.** 1 / at about 120 sccm oxygen flow is not quite clear yet.
The boron content of the layers show a slight increase with higher oxygen flow.

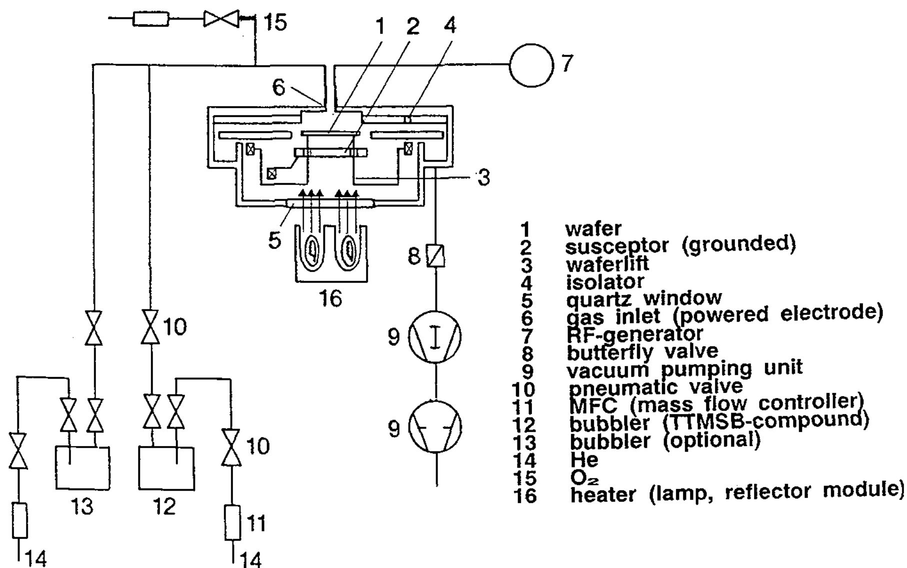


Fig. 1 : Schematic of PECVD-reactor

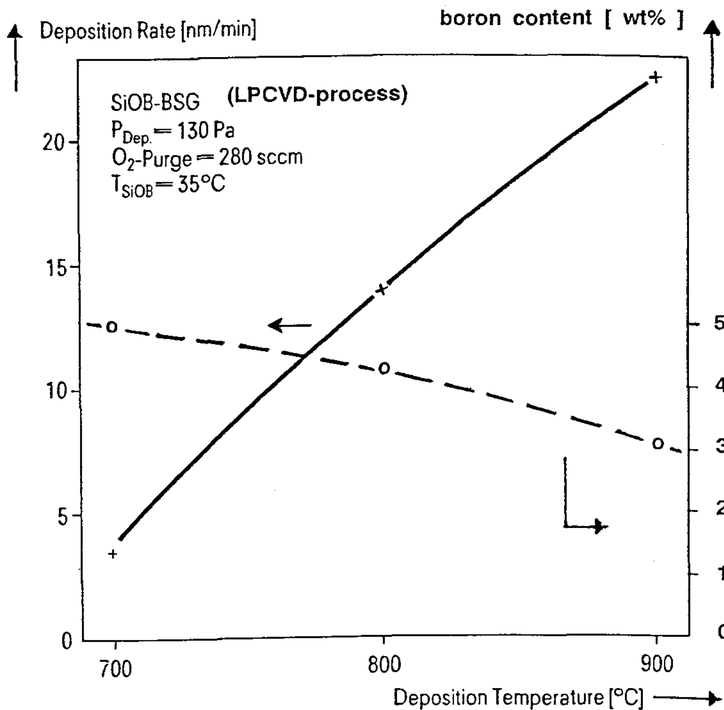


Fig 2 : Influence of the deposition temperature (LPCVD-process) on the deposition rate and the boron weight fraction for TTMSB-BSG

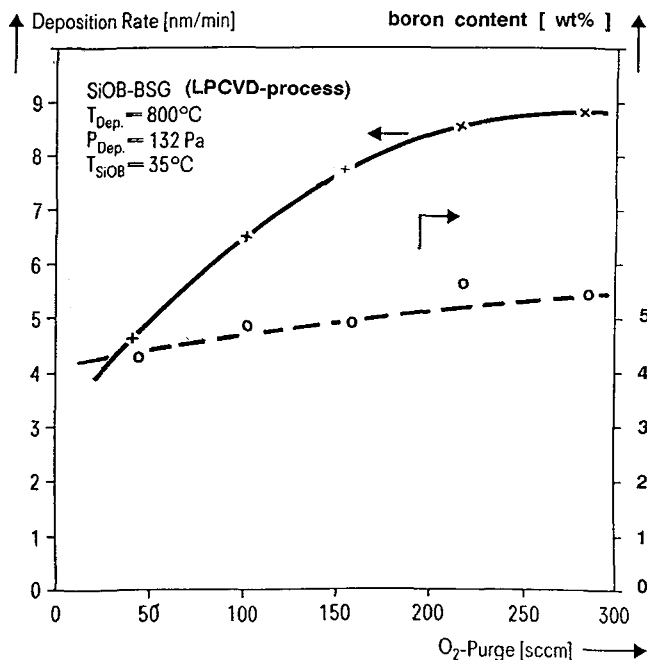


Fig 3 : Influence of the oxygen flow (LPCVD-process) on the deposition rate and the boron weight fraction for TTMSB-BSG

No influence of deposition pressure on the boron content could be determined.

In summary, the great advantage of the LPCVD-process is that the boron content in the layers changes only within small limits by varying the process parameters. This means that the pre-programmed boron content of theoretical 4.64 wt% (in TTMSB) is transferred to the deposited BSG-layers. No pile-up after diffusion near the BSG/silicon interface could be measures by SIMS. The process window is broadened compared to the TEOS-BSG-process.

## 2. PECVD-process :

No influence of oxygen and spacing of the electrodes on the deposition rate could be found. The growth rate can drastically be enhanced by increasing the TTMSB-carrier gas flow and slightly with higher RF-power and process pressure. The deposition rate slightly decreases with higher susceptor-temperature (see fig. 4, 5, 6).

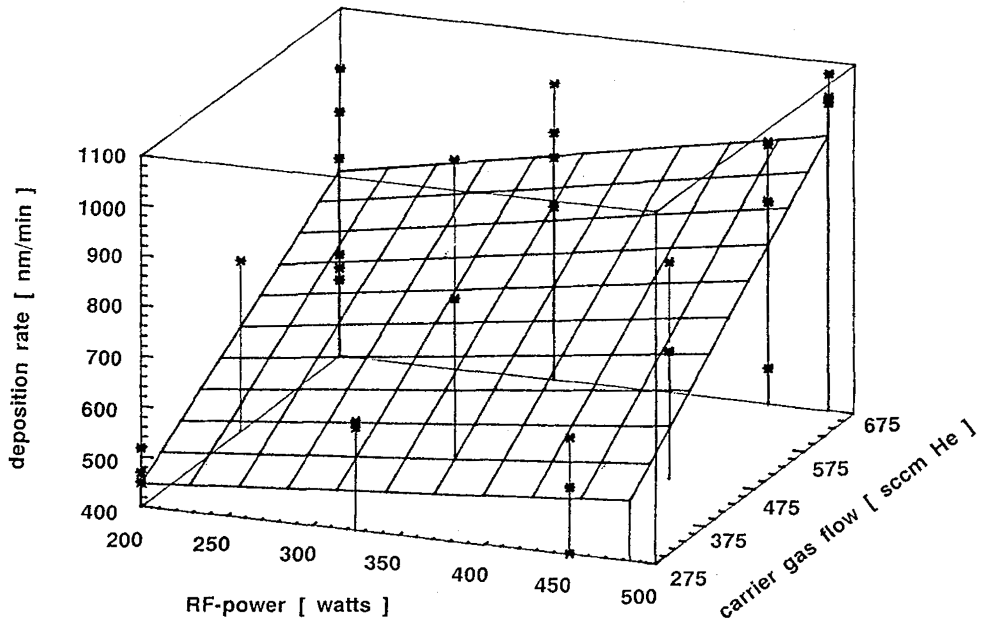


**Fig 4 : Influence of RF-power and TTMSB-carrier gas flow on the deposition rate of TTMSB-PECVD-BSG**

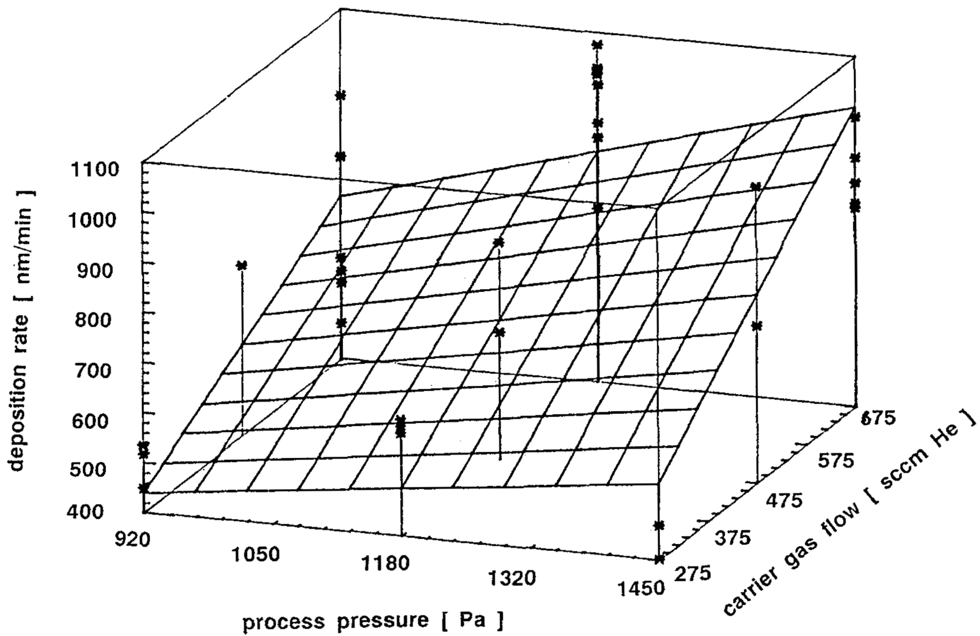


**Fig 5 : Influence of process pressure and TTMSB-carrier gas flow on the deposition rate of TTMSB-PECVD-BSG**

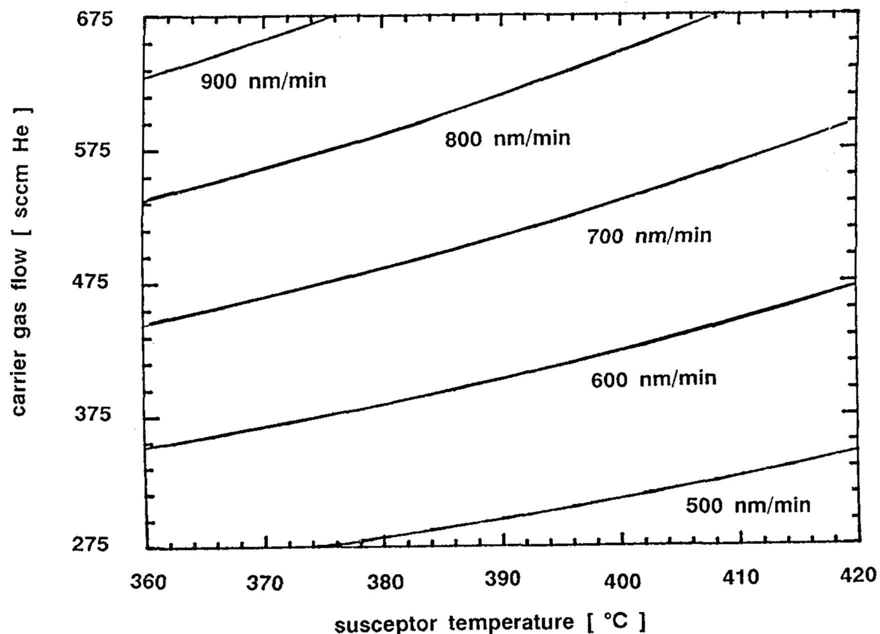


Fig 6 : Influence of susceptor temperature and TTMSB-carrier gas flow on the deposition rate of TTMSB-PECVD-BSG

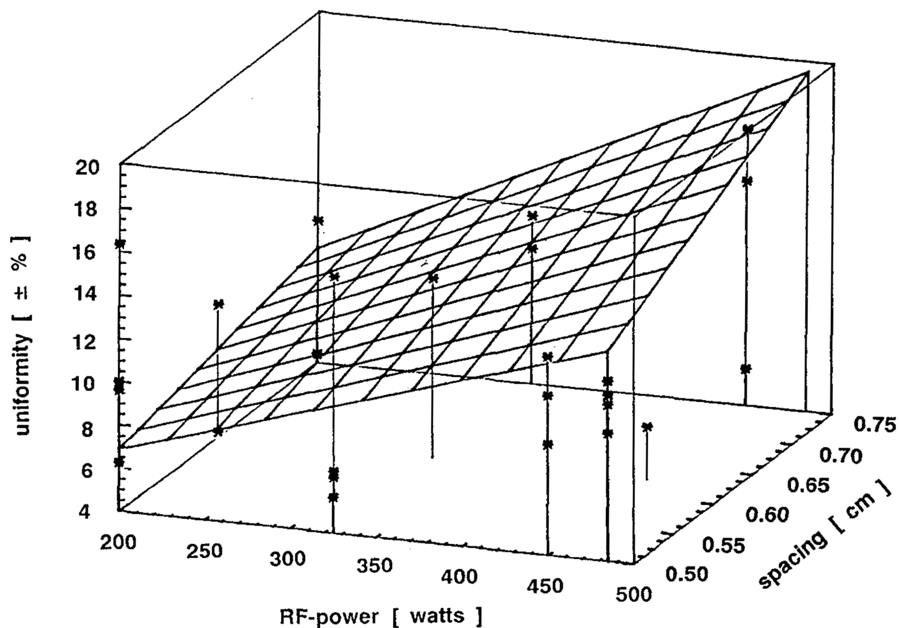


Fig 7 : Influence of RF-power and electrode spacing flow on the thickness uniformity of TTMSB-PECVD-BSG over 100 mm wafer

The film-thickness uniformity can be improved by reducing the RF-power and the electrode spacing (see **fig.** 7). Furtheron no influence of carrier gas flow, oxygen flow, deposition pressure and susceptor-temperature on thickness uniformity could be observed.

The main parameters influencing the boron weight fraction are until now not quite clear. A first result seems to be that with higher oxygen flow and a higher TTMSB-carrier gas flow the boron content in the BSG increases. The BSG-layers were characterized using FT-IR-measurements. **Fig.** 8 shows the influence of oxygen flow and carrier gas flow on the B-O-absorption peak at 1330 $cm^{-1}$. Accurate determinations of the boron content by ion-chromatography are not yet available.

The step coverage of the BSG-layers was measured with SEM . The step coverage is comparable to that BSG-layers yielded by PECVD-decomposition of TEOS together with TMB.

The composition of the layers analyzed by RBS (Rutherford back-scattering) show a silicon/oxygen ratio of 1/2.33.

The carbon contamination in layers with a boron content of 4.6 wt% (theoretical value given by the precursor TTMSB) is below 0.1 wt% C, the detection limit of NRA (nuclear reaction analysis).

Under extreme conditions (e.g. low susceptor-temperature, low RF-power, increased spacing and high oxygen-flow) the deposited material reveals a $Si-CH_3$-absorption peak at 1275 $cm^{-1}$ in FT-IR-spectra.

The PECVD-BSG-films are in environmental air as stable as BSG-layers deposited by LPCVD at 800 °C.

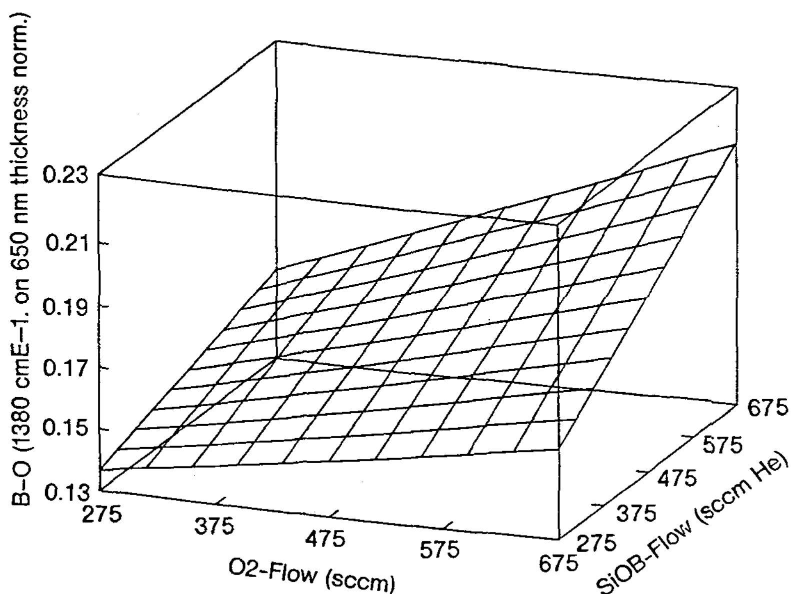


**Fig 8 :**

**Normalized B-O Absorption vs. SiOB- and $O_2$-Flow**

## Discussion

1. LPCVD-process :
Due to the fact that the glass formation process is quite completed at 800 °C / Lit. 1 / the formation of B-Si-bondings is not dominant. Thus no pile-up of boron near the BSG/silicon interface during heat-treatment could be measured.

2. PECVD-process :
Since there is only one molecule to collapse (TTMSB) one can speculate how the breakage of the bondings in the monomolecular precursor TTMSB can be initiated by varying e.g. the plasma energy. In spite of the limited information available and due to the different data on bonding energies, our estimations permit the conclusion that the dissociation kinetics of the different bondings in the molecule and hence their interactions with the growing glass layer are strongly influenced by the structure of the molecule in combination with the plasma-energy supplied. The theoretical boron weight fraction of 4.6 wt% given by the precursor molecule can be achieved, if the B-O or Si-O-bondings were not cracked in the plasma. This can be achieved by the following combination of process parameters :

- high process-pressure (e.g. 1300 Pa)
- high susceptor temperature (e.g. 420 °C)
- low RF-power (e.g. 325 W)
- low electrode spacing (e.g. 0.7 cm)

During the variation of process parameters within a statistical experimental design some layers were produced which were obviously built up by molecule fragments containing $Si-CH_3$-bondings (FT-IR-absorption at 1275 $cm^{-1}$; Aldrich catalogue of IR-spectra). The intensity of this sharp absorption peak varyied with the variation of the process parameters.

Some other parameter-combinations resulted in a complete removal of all nine $CH_3$-groups, leaving the desired SiOB-structure respectively "elementary-cell" to be built into the BSG-layer.

As a first result it could thus be shown that it is possible to produce BSG-layers of different compositions by cracking definite bondings in a given monomolecular precursor despite the mechanism is not yet understood and the knowledge about the energy supplied by a high-frequency plasma is not yet available.

## Conclusions

The novel BSG-processes using TTMSB described produce films of good qualities while eliminating problems like the regulation of the vapor pressures of different materials. As there is only one molecule to collapse, the monomolecular precursor TTMSB might be an ideal molecule to study how the breaking of definite bondings by varying the plasma parameters.
The processes are straightforward production orientated processes.
Whether the LPCVD-process or the PECVD-process is used in manifacturing semiconductor devices depends on the application needed. When BSG-layers are used as dopant-sources in combination with extreme device-geometries the LPCVD-process should be favoured because of its better step coverage. If low deposition temperatures are needed (e.g. for intermetal isolation) the plasma enhanced decomposition should be used.
The principle of "molecular engineering" seems to be a viable concept for improving CVD-processes in semiconductor technology.

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