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1 MHz dielectric constants of phosphosilicate glass films chemically vapour-deposited in the SiH_4–PH_3–O_2–N_2 system at low temperature

C. PAVELESCU*, D. SERGHI
R&D Centre for Electronic Components (CCSIT-CE), Str. Erou Iancu Nicolae 32B, R-72996 Bucharest, Romania

The a.c. relative dielectric constant (RDC) and resistivity of as-deposited and thermally annealed phosphosilicate glass (PSG) films with phosphorus concentrations in the range 0 to 9.3 wt% P were measured at a frequency of 1 MHz and at room temperature. The variations of RDC and resistivity with phosphorus concentration exhibit two regions: (i) for phosphorus concentrations in the range 0 to 4 wt% P, the RDC values of the as-deposited films are higher (above 4.5) than those of N_2-annealed films (around 3.5), while the resistivity values of the as-deposited films (around 4 MΩ cm) are lower than those of N_2-annealed-films (around 8 MΩ cm); and (ii) for phosphorus concentrations in the range 4 to 9.3 wt% P, RDC values of as-deposited films decrease to values below those of N_2-annealed films, while the values of resistivity of as-deposited and N_2-annealed films tend to the same value of 8.4 MΩ cm at concentrations above 8 wt% P. The behaviour of the RDC and resistivity of PSG films is interpreted in terms of (i) the evolution of a content of HO, H_2O, P–O and P=O polar groups as a function of phosphorus concentration and subsequent annealing processes, and (ii) the structural changes suffered by the films during subsequent annealing processes.

1. Introduction

The dielectric constants of chemically vapour-deposited SiO_2 films have been found to be strongly dependent on the deposition conditions and subsequent thermal annealing processes, and this behaviour was shown to be related to the H_2O and OH content of these films [1, 2].

On the other hand, phosphosilicate glass (PSG) films deposited in the SiH_4–PH_3–O_2–N_2 system at low temperature show a well-defined dependence of physico-chemical film properties as a function of phosphorus content and of thermal annealing processes [3–9]. Thus, the relative dielectric constant (RDC) and the breakdown voltage of PSG films prepared by different chemical vapour-deposition (CVD) methods vary with phosphorus concentration [3–5].

The behaviour of 1 MHz dielectric constants (RDC and resistivity) of PSG films deposited at low temperature was investigated in the SiH_4–PH_3–O_2–N_2 system against phosphorus concentration and annealing parameters (temperature and ambient), and to interpret the experimental data in terms of the evolution of polarizing species content and structural modifications of the films by the preparation conditions.

2. Experimental procedure

PSG films 150 to 200 nm in thickness with phosphorus concentration in the range 0 to 9.3 wt% P were deposited on silicon substrates in a Silox reactor (with standard nozzle) [6] at atmospheric pressure, at a temperature of 410 °C. The O_2/SiH_4 ratio was kept constant at 20 (SiH_4 flow rate of 38 $cm^3 min^{-1}$), the PH_3 flow rate was varied in the range 0 to 7.7 $cm^3 min^{-1}$, while the total flow (N_2-balanced) was kept constant at 9.8 $l min^{-1}$.

The film thickness was measured with an ellipsometer and phosphorus concentration in the PSG films was determined by using wet chemical etch-rate data [7]. The annealing was performed at temperatures in the range 600 to 1000 °C in dry N_2 or H_2O ambients. Also, a sample with 8 wt% P concentration was annealed for 150 h at 40 °C in a 93% H_2O relative humidity atmosphere.

MOS (metal-oxide-semiconductor) capacitors were fabricated on n-type silicon wafers of 4 to 6 Ω cm resistivity with PSG films used as a dielectric and with electron-gun-evaporated aluminium film of 1 μm thickness as electrode (sample area 0.84 mm^2). The capacitance and conductance of MOS capacitors were determined at room temperature by means of a digital LCR meter at a frequency of 1 MHz under a positive d.c. bias in order to cause carrier accumulation at the silicon surface. All experimental data were averaged for ten MOS capacitors on the same wafer.

The RDC, ε_r, and the resistivity, ρ, of PSG films were calculated from the following equations [8, 9]:

$$\varepsilon_r = Cd/\varepsilon_0 S \qquad (1)$$

* *Present address*: Applied Electronics Laboratory (AEL) No. 217, Stanford University, Stanford, CA 94305-4055, USA.

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$$\rho = S/Gd \qquad (2)$$

where C is the capacitance and G is the parallel conductance were measured at a frequency of 1 MHz, while S is the area of aluminium electrode, d is the film thickness and $\varepsilon_0 = 8.85 \times 10^{-12}\ \mathrm{F\,m^{-1}}$ is the permittivity of free space.

3. Results and discussion

3.1. General considerations

Vitreous quartz, thermal SiO_2 and chemically vapour-deposited SiO_2 films present similar infrared absorption spectra with characteristic absorption bands at wavenumbers of 1050, 800 and 440 cm^{-1} [10]. In fact, CVD SiO_2 films have an amorphous structure consisting of SiO_4 tetrahedra, similar to that of fused silica or thermally grown SiO_2 films [11].

On the other hand, PSG films with phosphorus concentration in the range 0 to 8 wt% P range present the characteristic absorption bands of fused quartz, and also a weak absorption band around a wavenumber of 1325 cm^{-1} which is assigned to the stretching vibration of the P=O bond [3, 4, 7, 10]. It should be mentioned that vitreous quartz, thermal SiO_2, CVD SiO_2 (deposited from SiH_4 and O_2) and PSG films with phosphorus content in the range 0 to 8 wt% P present refractive indices around 1.45 [4, 10, 12, 13] and densities in the range 2 to 2.2 $g\,cm^{-3}$ [4, 10]. Therefore, it may be concluded that the PSG films with concentration in the range 0 to 8 wt% P present an amorphous structure similar to that of fused quartz, although phosphorus incorporated in PSG films confers some characteristic behaviour of the film parameters such as stress, density, etch rate, infrared absorption spectra and refractive index [3, 4, 7, 10, 12–14]. It should be noted that CVD SiO_2 films deposited in the SiH_4–O_2–N_2 system at low temperature (250 to 400 °C) present RDC values in the range 3.8 to 6.5 when deposition and annealing conditions are varied [2]. PSG films deposited at low temperature by different CVD methods show values of RDC in the range 3.5 to 4.5 when the phosphorus concentration in the film is varied in the range 0 to 8 wt% P [4].

However, fused quartz, which is characterized by strong infrared absorption bands, shows a strong difference between the square of the refractive index ($n^2 = 2.13$) and its RDC value (3.85), this dielectric being classified as a polar material which exhibits principally atomic polarizability. The atoms of different kinds are frozen in the structure of the material and are not free to change their equilibrium positions [15]. Also, PSG films with concentration in the range 0 to 8 wt% P show values of n^2 and RDC [4, 12] similar to fused quartz [15]. In conclusion, PSG films with phosphorus concentrations in the range 0 to 9.3 wt% P will be considered in the following discussion as a polar dielectric, the interpretation of the behaviour of RDC and resistivity of PSG films being given in terms of the evolution of the content of chemical inpurities in PSG films, such as H_2O, OH and P–O polar groups [16] with phosphorus concentration and annealing conditions.

In the following discussion we take into consideration a qualitative rule which applies for large molecules: the dipolar molecular groups (OH, P–O etc.) contribute the same dipole moment in whatever molecule they occur [17].

3.2. Dependence of RDC of PSG films on phosphorus concentration and annealing conditions

It is well known that PSG films CVD-deposited in the SiH_4–O_2–PH_3–N_2 system at low temperature contain chemical impurities such as H_2O (physically adsorbed), OH (from the SiOH (silanol) group) and phosphorus incorporated in the P=O state [3, 4] or P–O state (substitutional state) due to a phosphorus atom substituting for silicon in SiO_4 tetrahedra [18]. The ratio of the dipole moment of water ($\mu_{H_2O} = 1.84$ debye) to that of the hydroxyl group ($\mu_{HO} = 1.5$ debye) is about $\mu_{H_2O}/\mu_{HO} = 1.2$, and it should be mentioned that the RDC of water is 78.2 [16]. Thus, the presence of H_2O and OH polar groups in CVD–PSG films with a phosphorus concentration of 4.3 wt% P [4], and also in CVD SiO_2 films [19], may explain the value of RDC of as-deposited PSG films of 4.5, at phosphorus concentrations in the range 0 to 4 wt% P (Fig. 1a, curve 1), these values of RDC being higher than that of about 4 for thermally grown SiO_2 or 3.8 for CVD SiO_2 films densified at 1000 °C in dry N_2 [2]. On the other hand, for PSG films with phosphorus concentrations in the range 4 to 8 wt% P the water or silanol content decreases strongly with increasing phosphorus concentration [7]; thus the RDC of PSG films decreases from 4.85 to 3.75 when the phosphorus content increase from 4 to 8 wt% P (Fig. 1, curve 1).

The lower values of RDC (around 3.6) of 0 to 4 wt% P-doped PSG films annealed in dry N_2 at 800 °C in comparison with values of about 4.5 obtained for as-deposited films (Fig. 1a, curves 1 and 2) may be interpreted in terms of H_2O and OH polarizing species removal from as-deposited films during annealing [20].

On the other hand, the P–O group (in which a phosphorus atom transfers one electron to an oxygen atom) has a strong polar character, with a dipole moment $\mu_{P\text{-}O} = 2.7$ debye ($\mu_{P\text{-}O}/\mu_{OH} = 1.8$) [16] and it may be expected that the P=O group (in which the phosphorus atom transfers two electrons to the oxygen atom) also presents a strong dipole moment. Thus, the increase of RDC of PSG films annealed in dry N_2 at 800 °C at phosphorus concentrations above 4 wt% P (Fig. 1a, curve 2) may be explained by the increase of content of P=O bonds in comparison with as-deposited films [7], and also by the increase of the content of P–O polar groups with phosphorus concentration in the PSG films.

The moderate effect of phosphorus concentration on the RDC of PSG films annealed in dry N_2 may be interpreted as follows. The incorporation of phosphorus in PSG films as PO_4 groups, with phosphorus substituting for a silicon atom in a SiO_4 tetrahedron [18, 21], can cancel the dipole moment of a PO_4

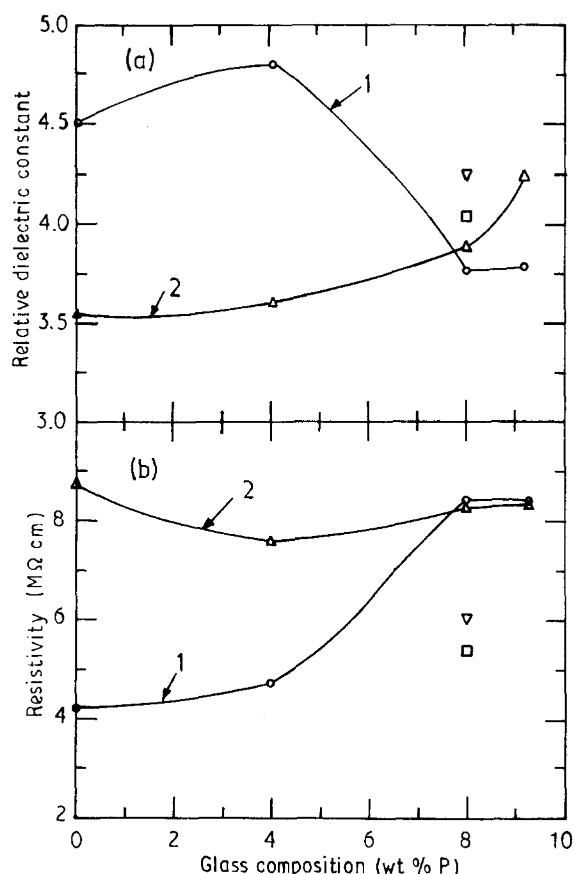
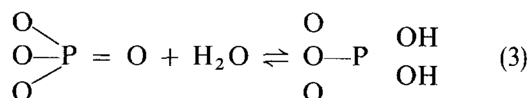


Figure 1 (a) Relative dielectric constant variation against glass composition for PSG films deposited in the SiH_4–O_2–PH_3–N_2 system at atmospheric pressure ($T_d = 400\,°C$, $F_{SiH_4} = 38\ cm^3\,min^{-1}$, $F_{PH_3} = 0$ to $7.7\ cm^3\,min^{-1}$): (○) curve 1, as-deposited films; (△) curve 2, films annealed at 800 °C in dry N_2 for 30 min; (□) 8 wt % P-doped PSG films annealed in steam at 600 °C for 30 min; and (▽) 8 wt % P-doped PSG films annealed at 40 °C in 90% H_2O relative humidity for 150 h. (b) Resistivity variation against glass composition with the same parameters and symbols as in (a).

group which is the sum of four dipole moments of four P–O dipoles oriented from the phosphorus atom to the vertices of the tetrahedron. However, in a PO_4 tetrahedron the four bonds are not equivalent, one of them being shorter [21] and thus the sum of the four dipole moments of P–O bonds is different from zero, the PO_4 group being characterized by a dipole moment probably much smaller than that of H_2O, OH, P–O and P=O polar species. Also, phosphorus incorporated in PSG films in the P–Si state (interstitial state) [18] may coordinate oxygen atoms in such a way that a net dipole moment may result. Thus, the relatively small effect (in comparison with that of HO and H_2O groups) on the RDC of phosphorus incorporated in PSG films may be interpreted in terms of a lower dipole moment of the P–O_4 group in comparison with that of HO, H_2O, P–O and P=O polar species.

On the other hand, water incorporation in 8 wt % P-doped PSG films during annealing in 92% relative humidity water vapour at 40 °C for 150 h may account for the higher value of RDC of 4.25 in comparison with that of 8 wt% P-doped as-deposited PSG films of 3.7 (Fig. 1a), due to H_2O incorporation in the PSG films as OH polarizing species, according to the reaction [20]:



$$(O)_3P{=}O + H_2O \rightleftharpoons (O)_3P(OH)_2 \qquad (3)$$

Also, the incorporation of water (according to Equation 3) in 8 wt% P-doped PSG films annealed for 0.5 h at 600 °C in steam may explain the slightly higher value of RDC of 4.1 in comparison with the value of 3.77 for 8 wt% P-doped as-deposited PSG films.

It should be concluded that the RDC of PSG films is strongly influenced by the evolution of HO and H_2O polar group content in the structure of PSG films during deposition and annealing in different ambients, and also by the evolution of P–O and P=O polar group contents during thermal annealing in dry N_2 with phosphorus concentration.

The effect of the annealing temperature in dry N_2 for 0.5 h on the RDC of 8 wt% P-doped PSG films is analysed next. The value of RDC of 3.74 obtained for 8 wt% P-doped PSG films annealed in dry N_2 at 600 °C (Fig. 2b) is similar to the value of 3.75 obtained for as-deposited films of the same phosphorus concentration (Fig. 1a), this fact denoting that 8 wt% P-doped as-deposited PSG films do not contain water or OH groups, which may be removed from the film by an annealing for 10 min in dry N_2 at 640 °C [20]. On the other hand, it should be stressed that the 8 wt% P-doped PSG films annealed in dry N_2 at 600 °C present an RDC value of 3.74 (Fig. 2b) which is lower

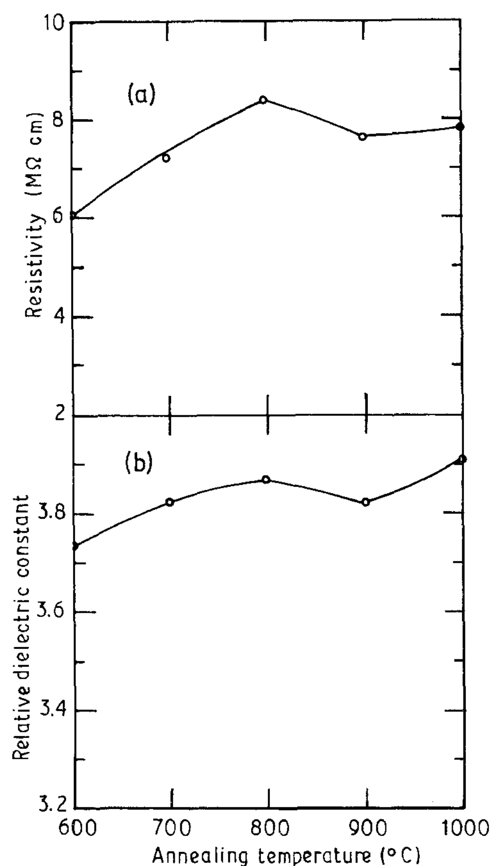


Figure 2 (a) Resistivity variation and (b) relative dielectric constant variation against annealing temperature in dry N_2 for 8 wt % P-doped PSG films.

than the value of 4.1 obtained for the RDC of 8 wt% P-doped PSG films annealed in H_2O at 600 °C (Fig. 1a), this fact denoting the incorporation in PSG films of polar species such as H_2O or OH groups according to Equation 3.

However, the RDC values of 8 wt % P-doped PSG films annealed in dry N_2 at temperatures of 700 and 800 °C show a small increase to 3.82 and 3.86 respectively, in comparison with the value of 3.75 for the RDC of as-deposited PSG films with the same phosphorus concentration (Fig. 2b); this variation is assigned to the increased content of P=O and P–O polar bounds in PSG films with increasing annealing temperature [7], which may increase the RDC of PSG films annealed in dry N_2.

However, the RDC of 8 wt% P-doped PSG films annealed in dry N_2 at 900 °C experiences a small decrease to 3.82 in comparison with 3.87 obtained for films annealed at 800 °C, while for an annealing temperature of 1000 °C the RDC increases to 3.91 (Fig. 2b). This behaviour of 8 wt % P-doped PSG films may be interpreted in terms of reflow phenomena which appear at temperatures above 900 °C [22], and may determine a significant change in the structure of 8 wt% P-doped PSG films. This can also exert an influence on the content of P–O and P=O polar bonds which can affect the RDC of PSG films annealed in dry N_2 at temperatures above 900 °C.

3.3. Dependence of resistivity of PSG films with phosphorus concentration and annealing conditions

The dielectric losses in thin films of amorphous dielectrics such as Si_3N_4, SiO and Al_2O_3 are characterized by a strong increase of film conductivity with frequency. This behaviour was previously interpreted in terms of electronic hopping motion which corresponds to thermally assisted tunnelling between discrete sites, as distinct from transport of effectively free carriers in the valence and conduction bands of conventional crystalline conductors and semiconductors [23, 24]. It should be mentioned that the values of conductivity of evaporated SiO and anodized Al_2O_3 thin films measured at a frequency of 1 MHz are about 10^{-6} Ω^{-1} cm^{-1} (resistivity of 1 MΩ cm) [24]. It should be noted that PSG films, which also present an amorphous structure similar to CVD SiO_2 films show a resistivity in the range 4 to 9 MΩ cm when measured at a frequency of 1 MHz (Fig. 1b), similar to the values of resistivity of SiO and Al_2O_3 thin films measured at the same frequency [24]. Therefore, it may be concluded that in PSG films with phosphorus concentrations in the range 0 to 8 wt% P, the conduction mechanism may be interpreted in terms of electronic motion which corresponds to thermally assisted tunnelling between distinct sites separated by small energy gaps and grouped in distinct bands in the forbidden band; these are separated from each other or from the edges of conduction or valence bands by higher energy gaps which represent bottlenecks for the conduction process [23]. Thus, the behaviour of the resistivity of PSG films will be interpreted in terms of the evolution of the number of sites which permit the electronic hopping motion as a function of phosphorus concentration and annealing conditions. The number of sites in PSG films which permit electronic conduction is considered to originate from the presence of chemical impurities (such as OH and H_2O groups) or from dangling bonds of oxygen, silicon and phosphorus atoms in CVD PSG films.

As-deposited SiO_2 films have an unstable structure, the arrangement of SiO_4 tetrahedra being more irregular than in heat-treated films [11]. As-deposited SiO_2 films also contain chemical species such as H_2O and OH, while these species are removed from the film during annealing in dry N_2 [20]. Thus, it is expected that as-deposited SiO_2 films present a higher number of active sites for electronic hopping motion than SiO_2 films annealed at a temperature of 800 °C in dry N_2. This model explains the higher value of resistivity of 8.8 MΩ cm obtained for SiO_2 films annealed in dry N_2, in comparison with the value of 4.2 MΩ cm obtained for as-deposited SiO_2 films (Fig. 1b, curves 1 and 2).

The small increase of resistivity of as-deposited PSG films with phosphorus concentration in the range 0 to 4 wt % P (Fig. 1b, curve 1) indicates that the structure of these films is not influenced by phosphorus incorporation. Thus, the higher number of active sites for electronic hopping motion, which can be correlated with the presence of OH and H_2O polarizing species [4, 19] in as-deposited PSG films with phosphorus concentration in the range 0 to 4 wt % P, may explain the lower values of resistivity of about 4.5 MΩ cm in comparison with the resistivity of about 8 MΩ cm of nitrogen-annealed PSG films with the same phosphorus concentration (Fig. 1b, curves 1 and 2).

The increase of resistivity of as-deposited PSG films from 4.7 to 8.4 MΩ cm when the phosphorus concentration in the PSG films increases in the range 4 to 8 wt % P (Fig. 1b, curve 1) may be associated with the decrease of HO and H_2O polar species content in as-deposited films [7]. Also, the small variation of resistivity of PSG films annealed in dry N_2 at 800 °C from 7.6 to 8.4 MΩ cm when the phosphorus concentration increases in the range 4 to 8 wt % P (Fig. 1b, curve 2) may be associated with the elimination of OH and H_2O polar groups from the PSG films during annealing [20] and with the small effect of phosphorus concentration on the resistivity of N_2-annealed PSG films. It should be mentioned that at concentrations of 8 wt % P or greater the resistivity remains essentially constant at a value of about 8.4 MΩ cm, both for as-deposited and N_2-annealed PSG films (Fig. 1b). On the other hand, the resistivity value of 8.4 MΩ cm for 8 wt % P-doped as-deposited PSG films (Fig. 1b, curve 1) decreases to 6 MΩ cm for films annealed at 40 °C in 92% relative humidity water vapour for 150 h, and to 5.4 MΩ cm for films annealed in steam at 600 °C (Fig. 1b), this behaviour being correlated with H_2O and OH incorporation in PSG films during annealing in ambients containing water, according to Equation 3. Therefore, it may be concluded that the

incorporation in PSG films of H_2O and OH polarizing species during deposition or annealing in ambients containing water leads to an increase in the number of active sites for electronic hopping motion, and thus a decrease of resistivity is noticed, in comparison with N_2-annealed or 8 to 9.3 wt% P-doped as-deposited PSG films from which H_2O or OH species are removed during annealing or deposition, respectively.

The tensile stress of 8 wt% P-doped as-deposited PSG films becomes a compressive stress after 30 min of annealing in dry N_2 at 600 °C [4], this behaviour indicating a significant compaction and structural change of the PSG films during N_2 annealing; the increase in the number of dangling bonds of silicon, oxygen and phosphorus atoms determines a higher number of active sites for electronic hopping motion with respect to as-deposited PSG films, and thus a lower value of resistivity of 6 MΩ cm is noticed for 8 wt% P-doped PSG films annealed in dry N_2 at 600 °C (Fig. 2a) in comparison with the resistivity of 8.4 MΩ cm of as-deposited films with the same phosphorus concentration (Fig. 1b).

On the other hand, heat treatment in dry N_2 at temperatures above 700 °C densifies the PSG films (the etch rate decreases, and its resistance to water absorption increases [20]), which leads to more compact PSG films with a small number of dangling bonds of phosphorus and oxygen atoms. Thus the small number of active sites for electronic hopping motion which are present in the films accounts for the increase of resistivity of 8 wt% P-doped PSG films when the temperature increases in the range 600 to 800 °C (Fig. 2a). However, the decrease in resistivity of 8 wt% P-doped PSG films annealed in dry N_2 from 8.4 MΩ cm at 800 °C to 7.6 MΩ cm at 900 °C and to 7.8 Ω cm at 1000 °C (Fig. 2a) may be explained in terms of reflow phenomena which appear at temperatures above 900 °C [22]. This may determine a significant change in the structure of the films which can increase the number of active sites for electronic hopping motion, and therefore the resistivity of the PSG films decreases.

4. Conclusions

PSG films with phosphorus concentrations in the range 0 to 9.3 wt% P may be considered as a polar material which exhibits principally atomic polarizability.

The relative dielectric constant of PSG films is strongly influenced by the evolution of content of HO, H_2O, P–O and P=O polar groups as a function of phosphorus concentration and subsequent thermal annealing in different ambients.

The behaviour of the resistivity of PSG films is interpreted in terms of the variation in the number of active sites for electronic hopping motion as a function of the evolution of OH, H_2O and phosphorus content in the film during the deposition process and subsequent annealing.

The structural changes suffered by PSG films during subsequent thermal annealing influence the values of dielectric parameters of these films.

It may be concluded that an increase in the content of OH and H_2O polar species in PSG films determines the increase of relative dielectric constant and the decrease of resistivity, while the influence of phosphorus content on the dielectric parameters of PSG films takes place in a complex manner, both by forming P–O and P=O polar groups in the film and by influencing the process of incorporation of OH and H_2O in the film during deposition or annealing in ambients containing water.

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