Comparison of open volumes in silica based thin films produced by different precursors

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Abstract. Silica thin films were deposited by spin coating on p-type (100) Si substrate and depth profiled with Positron Annihilation Spectroscopy (DP-PAS). A first series of samples were produced from precursor gel with molar ratio HSi(C₂H₅O)₃ [≡TES] : (CH₃)HSi(C₂H₅O)₂ [≡MDES] : H₂O : EtOH = 1 : 1 : 5 : 5. Samples were thermally treated in air at temperatures up to 600 °C. The structure and the chemical environment of the open volumes of these samples were compared with the ones of a previous studied second series of films obtained by hydrolysis and condensation reaction of Tetraethylorthosilicate (TEOS). The effects of sol precursors and thermal treatment temperature on open volumes were studied by Doppler broadening spectroscopy and detection of 3γ-annihilation of ortho-positronium. The introduction of CH₃ groups by MDES produces an open disordered structure whose decoration of H atoms gives rise to a very high S parameter (1.076) but with very low positronium 3γ-annihilations.

1. Introduction
In the last years, silica-based porous materials have been widely studied for their huge range of applications such as low refractive index materials for optical coatings, low-dielectric constant (low-k) films for microelectronic applications and membranes for separation, catalysis and chemical sensing [1].

Materials with low refractive index are interesting for possible applications ranging from optical materials and display devices, to solar cell coatings in order to increase transmittance and decrease the reflection. One promising way of reducing the refractive index is the reduction of the material density by introduction of porosity [2]. The introduction of porosity leads also to a reduction of the dielectric constant of a given material. Actually, insulators with a dielectric constant lower than the conventional SiO₂ (k~4) are used to improve the performance of integrated circuits [3, 4].

Nano-porous amorphous silica films deposited on porous support (pore sizes larger than some microns) exhibit good gas filtering characteristics. In these films the presence of a network of sub-nanometer pores separate the components of a gas mixture by a molecular sieving effect. Applications range from the field of production of pure molecular hydrogen [5-7] to the separation of CH₄ in biogases [8]. Silica based materials are also used in the purification of deoxyribonucleic acid (DNA) from biological samples. DNA molecules are selectively adsorbed by Coulombic force while contaminants are washed away by organic solvents [9].

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In these applications the porosity plays a fundamental role, therefore the characterization of the distribution, the size, the shape and the interconnectivity of the pores is extremely important. Few analytical techniques are available to extract this information [3]. DP-PAS has been shown to be one of the most sensitive tools to probe pores identifying their distribution, size and interconnectivity [4, 10, 11]. Positrons injected in a solid, after thermalization with the medium and a diffusion path, annihilate in two 511 keV gamma rays with an electron of the host. Due to its positive charge positron is mainly localized in the open volumes of the solid where the annihilation with the low momentum electrons produces a narrowing of the 511 keV annihilation line [12].

In insulators, due to their open structure, positron can also form a positronium (Ps) atom. In vacuum Ps is formed for 1/4 as para-positronium (p-Ps) that annihilates in two gamma rays with a lifetime of 125 ps and 3/4 as ortho-positronium (o-Ps) that annihilates in three gamma rays after 142 ns. In a solid o-Ps can also annihilate with an electron of the medium (pick-off process) in two gamma rays and its lifetime is shortened to a few nanoseconds. In presence of interconnected porosity, o-Ps can out-diffuse towards the surface and eventually be emitted into the vacuum [11].

The probability of pick-off annihilation and the shape of the 511 keV gamma annihilation peak is influenced by the pore sizes and by the chemical termination of the pore walls [13, 14]. Because o-Ps and positron are very sensitive to the local environment of the annihilation site, it is fundamental to know the annihilation properties to define the open volumes dimension and concentration. The lack of this information can hinder a direct correlation both of the $3\gamma - 2\gamma$ ratio and the width of 511 keV annihilation peak with the open volume size.

In this work we present DP-PAS measurements on silica based porous thin films deposited by spin coating on Si substrate. In particular the morphology and the chemical environment of the open volumes are analyzed and compared for two series of samples obtained using as precursors Triethoxysilane (TES)-Methyldiethoxysilane (MDES) and Tetraethylorthosilicate (TEOS), respectively. While TEOS precursor has been shown to give pure silica films after annealing above 500 °C [7], films deposited using MDES are expected to contain CH$_3$ groups. As CH$_3$ groups in SiO$_2$ structure are organized in long chains with different cross-linking [3], they are expected to generate more open free volumes compared to silica [4]. The walls of the free volumes would be H terminated [4, 14].

### 2. Experimental

Silica thin films were deposited by spin coating on p-type (100) Si substrates and thermally treated in air at temperatures up to 600 °C. The silica sols, for the deposition of the first series of film, was prepared dissolving Triethoxysilane (TES) and Methyldiethoxysilane (MDES) in absolute ethanol (EtOH). The molar ratio was TES : MDES : H$_2$O : EtOH = 1 : 1 : 5 : 5. Films were deposited after 24 h from the precursor preparation and, after deposition, the films were baked at 125 °C. Two samples were successively annealed in static air at 300 and 600 °C for 60 min using a heating rate of 1 °C min$^{-1}$. The samples treated at 125 °C, 300 °C and 600 °C will be referred as #1, #2 and #3, respectively. The thicknesses of these films ranged from 350 to 500 nm.

The second series of silica films was prepared by hydrolysis and condensation reaction of Tetraethylorthosilicate (TEOS) in presence of water and ethanol. The molar ratios were TEOS : H$_2$O : EtOH : HNO$_3$ = 1 : 6 : 6 : 0.01 (sample #4) and 1 : 6 : 6 : 0.1 (sample #5). A third sample was produced adding Polyvinylpyrrolidone (PVP) as porogen with molar ratio TEOS : H$_2$O : EtOH : HNO$_3$ : PVP = 1 : 6 : 6 : 0.1 : 1 (sample #6). After deposition, samples #4, #5 and #6 were baked at 125 °C and then thermally treated at 600 °C for 60 min using a heating rate of 1 °C min$^{-1}$. Data of samples #4 and #5 are the same as in Ref. [7] while sample #6 was analyzed in Ref. [15-17].

The Doppler broadened 511 keV positron annihilation line was measured as a function of the positron implantation energy $E$ in the energy range 50 eV - 25 keV. $E$ was related to the mean positron implantation depth $z$ through the relation $z = (40/\rho) E^{1.6}$. In this relation $z$ is in nm when the density $\rho$ is expressed in g/cm$^3$ and $E$ in keV. For silica films a density of 2.2 g cm$^{-3}$ has been used. The measurements were carried out with a slow positron beam [18] equipped with two high purity
germanium detectors with 1.4 keV resolution at 511 keV. The annihilation peak was characterized by the shape parameter $S$ calculated as the ratio of the counts in the $|511 - E_{\gamma}| \leq 0.85$ keV central area to the total area of the peak ($|511 - E_{\gamma}| \leq 4.25$ keV) and the wing parameter $W$ calculated as the fraction of the counts in the region $1.6 \leq |E_{\gamma} - 511| \leq 4$ keV. $E_{\gamma}$ is the energy Doppler shift of the annihilation $\gamma$-ray. The $S$ and $W$ parameters were normalized as $S_n = S_{\text{measured}}/S_{\text{bulk-Si}}$ and $W_n = W_{\text{measured}}/W_{\text{bulk-Si}}$.

The VEPFIT program, [19] based on the solution of the diffusion equation, was used to extract from the $S_n(E)$ and $W_n(E)$ curves the characteristic ($S_n$, $W_n$) values of the films. The $S_n(E)$ and $W_n(E)$ curves of samples #1, #2 and #3, were fitted with three layers (film, interface of a few nanometers and Si substrate).

The $3\gamma - 2\gamma$ ratio [$R(E)$ parameter] was calculated as the ratio between the valley area ($E_{\gamma}$ between 410-500 keV) and the 511 peak area. The $R(E)$ parameter was calibrated by measuring the Ps formation in a Ge crystal as a function of the temperature. The $R_n(\%)$ calibrated parameter is defined as $(R(E)-R_0)/(R_{100}-R_0)$. Where $R_{100}$ (100% Ps formation) is assumed as the $R$ value obtained by extrapolating to zero implantation energy the $R(E)$ curve measured in Ge at 1000 K [20] where all positrons reaching the Ge surface form Ps [21]. Because in the Ge bulk positrons do not form Ps, as $R_0$ (0% Ps formation) the $R$ value at the highest positron implantation energy was assumed.

3. Results and discussion

In figure 1 the $S_n(E)$ curves of the measured samples are reported. The samples produced using TES and MDES as precursors (#1, #2 and #3) show very high $S_n$ values in the film region (below $E_{\gamma}$=6-7 keV) if compared with samples obtained by TEOS (#4, #5 and #6). The fitted $S_n$ values characteristic of the films #1, #2 and #3 have been found to be 1.056, 1.054 and 1.076, respectively. These values are much higher also than that of the sample #6 ($S_n = 1.012$) that is rich of pores after removal of PVP porogen. In this sample the total porosity was estimated to be around 58% [17] and the pore size was evaluated to be $d \geq 2.0$ nm [15].

![Figure 1. $S_n$ parameter vs. positron implantation energy $E$.](image)

$R_n(\%)$ vs. $E$ curves of all the measured samples (figure 2) points out a low $3\gamma - 2\gamma$ ratio in the films deposited starting from TES and MDES. $R_n(\%)$ in the #1 and #2 films is lower than 1%, in sample #3, $R_n(\%)$ value is slightly higher (~2%). These $R_n(\%)$ values point out a very low o-Ps self annihilation and they are comparable with those found in films #4 and #5. In these last samples the total porosity was estimated to be less than 30% by dielectric constant measurements [7], i.e. around the half of the porosity of sample #6 corresponding to a $R_n(\%)$~14% [15].

In figure 3 the ($S_n$, $W_n$) values characteristic of each film are shown. On the same figure, data of Ref. [7] indicating ($S_n$, $W_n$) values of films prepared with the same composition of the sol precursors
of #4 and #5 and annealed at different temperature up to 900 °C are reported. The dashed and continuous lines are linear fit through the points groups of the films realized with TEOS and TES+MDES, respectively. As discussed in Ref. [7] the position of each \((S_n, W_n)\) value on its line is given by the number and the size of open volumes present in the film that depend on the annealing temperature, while the chemical environment probed by positrons is characterized by the line parameters. The large difference in the behavior of dashed lines and continuous line indicates a considerably different chemical environment of the annihilation site.

![Figure 2](image1.png)

**Figure 2.** \(R_d(\%)\) parameter vs. positron implantation energy \(E\).

The very high \(S_n\) and very low \(W_n\) values of films #1 \([S_n, W_n] = (1.056, 0.991)\], #2 \([1.054, 0.989]\) and #3 \([1.076, 0.918]\) are a strong indication of the presence of H atoms around the positron annihilation sites in these films [4, 22, 23]. The low \(S_n\) and high \(W_n\) values observed in the films produced with TEOS are characteristic of the presence of O around the annihilation site.

The slight increase of \(S_n\) and \(R_d(\%)\) values of sample #3 with respect to samples #1 and #2 (figure 1 and 2) could be attributed to the loss, induced by the thermal treatment at 600 °C [4], of weakly bound H on the walls of the open volumes. This could call for an increase of the size of the open volumes in #3.

![Figure 3](image2.png)

**Figure 3.** Open circles and open squares are the characteristic \((S_n, W_n)\) values of films prepared with the same composition of #4 (full circle) and #5 (full square), respectively, and annealed at different temperature up to 900 °C. Dashed lines are their best fits. The continuous line is a linear fit through the experimental points of the samples #1, #2 and #3 (full triangles).

The experimental high \(S_n\) and low \(R_d(\%)\) values in the #1, #2 and #3 films are compatible with the presence of small open volumes decorated by H atoms. However DP-PAS measurements are not able
to exclude the presence of larger open structures where Ps is formed but o-Ps is completely quenched by pick-off. Remembering that, in silica films, from 30% up to 80% Ps is yield [24] and that CH₃ groups enhance the open free volumes with respect to pure silica films [4], a high Ps formation could be expected also in these films. In this case, a part of the observed high $S_0$ value could be attributed to p-Ps self annihilation and another part to the pick-off of o-Ps with H electrons.

In order to understand if positrons annihilate directly with electrons of hydrogen atoms or after Ps formation, positron annihilation lifetime spectroscopy (PALS) and total porosity evaluation by dielectric constant measurements are planned.

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