Orthopositronium annihilation and emission in mesostructured thin silica and silicalite-I films

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Mesoporous silica layers and silicalite-I pure silica zeolite films were investigated using slow positrons. Detection of the 3γ annihilation fraction was used as a quick test to estimate the emission of orthopositronium (oPs) into vacuum. Positronium time-of-flight (TOF) spectroscopy, combined with Monte-Carlo simulation of the detection system was used to determine the energy of oPs emitted from the layers. Evidence for an efficient oPs emission was found in both the silicalite-I layer and in mesoporous films. A 3γ fraction in the range of 31-36 % was found in the layers with the highest oPs yield in each type of porous material, indicating that 40-50 % of the implanted positrons form positronium in the pore systems with very different pore sizes. Time-of-flight measurements showed that the energy of the orthopositronium emitted into vacuum is below 100 meV in the film with approximately 2 nm pores at 3 keV positron energy, indicating an efficient slowing down but no complete thermalization in the porous layers of 300-400 nm thickness.

Keywords: positronium, Monte Carlo simulation, gamma-ray energy spectroscopy, time-of-flight, mesoporous silica, thin film, thermalization

PACS: 78.70 Bj

Presented at the 11th International Workshop on Slow Positron Beam Techniques for Solids and Surfaces (SLOPOS-11), 9-13 July 2007, Orléans, France

Submitted for publication in Applied Surface Science

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Introduction

Thin mesoporous and microporous silica layers are intensively studied systems with potential use as membranes, sensor components and templates for nanostructures as well as dielectrics for semiconductor devices. Self-assembled mesoporous layers with several nm pore size and different pore symmetries have been developed, using the sol-gel method [1].
Positron annihilation spectroscopy has been applied to study the pore size, porosity and pore interconnectivity in thin porous layers [2, 3]. Positrons implanted into SiO_2 structures with a porosity on the nanometer scale form positronium on the internal surfaces with high efficiency. In contrast with a SiO_2 single crystal or another dense solid, positrons in a porous system are in the vicinity of an internal surface at all time during their thermalization and therefore the probability that they form a positronium with an electron of the solid at an energetically favorable point is high. The positronium is born on the surface of a pore with approximately 1 eV energy and slows down via collisions with the internal surface as well as with physisorbed molecules and chemically bound surface groups [4].
In the case of a highly interconnected (open) pore system and a shallow positron implantation depth the positronium formed in the pores may reach the external surface of the layer and Ps emission into the vacuum may be observed. The potentially efficient reemission of slow positronium makes these layers possible candidates for the role of a positron-positronium converter to produce a positronium target cloud for positively charged antihydrogen ion generation [5].

Direct detection of the emitted orthopositronium and measurement of its energy is possible by using a time-of-flight (TOF) system which detects the self-annihilation of the emitted positronium at a given distance from the sample surface. Although the short-living singlet Ps, the parapositronium may also leave the layer, its contribution to the TOF signal is negligible due to the short lifetime (125 ps) and predominantly the triplet orthopositronium (oPs, with 142 ns vacuum lifetime) is detected. The easily measurable 3γ annihilation signal can be used to test the presence of orthopositronium in the system, although this parameter alone can give only limited information on the intensity of the positronium component and the oPs emission. Time-of-flight studies found positronium emission from porous silica layers at less than 100 meV at 3-4 keV positron beam energy [4]. However, no solid evidence has been found of a complete thermalization and the time-of-flight studies seldom estimate the positronium reemission probability.

Better knowledge on the interaction of positrons with porous systems is needed in order to apply positron annihilation spectroscopy as a probe of pore size, porosity and pore interconnectivity as well as to develop an efficient cold orthopositronium source for antihydrogen production. In the present work we study orthopositronium creation and emission in SiO_2 layers with different pore sizes.

Experimental

Three batches of samples have been studied. The 300-400 nm thick "C" films have been grown using the cationic surfactant CTACl (cetyl trimethyl ammonium chloride) as structuring agent and tetraethyl-orthosilicate (TEOS) as Si source, with the aqueous evaporation-induced self assembly (AEISA) method [6]. The CTACl/TEOS molar ratio changed between 0.04 and 0.40. Spin coating at 2000 rpm speed was used to deposit the layers on a glass substrate. The deposited layers have been dried in air overnight at 150 ˚C

and stored in air until the positron measurements. The surfactant was removed by heating the layers at 400 ˚C in air.

The approximately 700 nm thick "F" films have been grown using Pluronic® F-127 ethyleneoxide/propyleneoxide block copolymer (BASF). A mixture of F 127, TEOS, ethanol, deionized water and HCl in $x:1:8:8:5x10^{-5}$ molar composition (the molar ratio x being between 0.004 and 0.03) has been deposited by spin coating on glass at 2000 rpm speed. The porogen was removed by heating at 400 °C in air. In the following discussion, the F and C samples will be named by writing the molar ratio of the structuring agent after the abbreviation of the porogen (e.g. F 0.004).

A third batch of samples (Z) consists of 500-700 nm thick silicalite-I layers grown on glass. A gel with a molecular composition of $9TPAOH : 25SiO_2 : 480H_2O$ was prepared by mixing tetrapropylammonium hydroxide, sodium silicate powder and destilled water. The preparation of the substrate was performed using the procedure described in Ref. 7. The deposition of the silicalite layer was made at 100 ˚C, during 10 hours. After deposition the layers were calcinated at 550 ˚C in air.

In order to remove the absorbed water, all samples were heated at 450 ˚C in air prior to the positron measurements and mounted in the vacuum chamber within minutes after heating. 3 γ annihilation fraction measurements, based on the difference of the energy distribution of the annihilation photons in events yielding two and three photons [3], were performed at the magnetically guided slow positron beam system in Orleans, France. A high purity germanium detector with 25 % relative efficiency, placed perpendicularly to the beam direction detected the annihilation gamma photons. The fraction of impinging positrons annihilating through 3 γ photons ($I_{3\gamma}$) has been determined from the measured positron spectra. $I_{3\gamma}$ was calibrated using the observed change in the intensity of the 2 γ annihilation peak. Orthopositronium time-of-flight measurements have been performed at the Linac-based slow positron beam in Tsukuba, Japan [8].

Results and discussion

The glass substrate used did not show any significant 3 γ annihilation component above 1 keV positron beam energy, and has a very short positron diffusion constant, therefore the orthopositronium signal can be attributed exclusively to oPs formed from positrons implanted into the porous layer. In Fig. 1 the 3 γ annihilation fraction as a function of the positron beam energy is plotted for samples from the F series with two different porogen/silicon ratio. At lower porogen content (F 0.004 sample) a value of 20 % at low energy was found that corresponds to an efficient oPs emission from the pores in the vicinity of the external surface. The curve shows a slight plateau of 13 % at 2-4 keV energy (this feature can be found in other layers with low porogen content as well). The plateau can be attributed to oPs that annihilate in the pores of the film. It can be concluded that the pore interconnection is low at this F-127 ratio and no significant amount of oPs can reach the surface from the e^+ implantation depth corresponding to 3 keV energy. A qualitatively similar effect was found in the case of C samples grown with lower porogen ratio as well.

At higher F127 molar ratio (F0.014 layer) a well defined plateau with 30 % 3 γ annihilation fraction is visible between 1-4 keV positron energy. The high 3 γ value can be explained by orthopositronium annihilation in the pores. However, as the long orthopositronium lifetime in a mesoporous layer grown using F127 is 60-70 ns [9], the corresponding intensity of this

lifetime component would be approximately 60 % ($I_{3\gamma}\tau_{oPs}/\tau$ where τ_{oPs} is the 142 ns oPs lifetime and $I_{3\gamma}$ is the 3 γ fraction) to explain the observed 3 γ effect. This value would be unusually high. Another possible explanation for the high 3 γ signal from the plateau is to expect a high degree of pore interconnectivity in the film and consequently a (nearly) complete emission of the oPs that are born in the pore system. This model puts the intensity of the oPs component to 30 %. In the case of the F-0.004 film no positronium emission into the vacuum is expected above 3 keV and the oPS intensity in the pores can be estimated as 26 %.

On Figure 2 positron 3 γ annihilation spectra of three porous films with different pore size are shown. We expect in all three cases oPs emission into the vacuum. The case of the F-0.014 film has been discussed above. On the basis of the approximately 2 nm pore diameter in the C-0.22 layer [10], an oPs lifetime of 30 ns is expected [2]. The measured 36 % 3 γ intensity would require a trapped othopositronium intensity of 170 % which is an obvious contradiction, leaving the oPs emission into the vacuum as the only possible explanation for the measured effect. The same argument holds for the silicalite-I sample as well, where the largest diameter of the channels is less than 1.1 nm. Evidence of an efficient orthopositronium emission from the channel structure of silicalite-I has been found earlier by conventional positron lifetime studies, by detecting oPs annihilation with a lifetime near the vacuum value at high intensity in silicalite powder samples [11, 12].

A remarkable common feature of the three spectra is the similar, 31-36 % amplitude of the 3 γ annihilation signal. The similarity implies that the positron/positronium branching ratio is nearly identical, independently of the pore structure. Taking into account the 25 % parapositronium which decays with 2 γ photons and which is consequently not counted in the 3 γ annihilation fraction measurement, the branching ratio can be estimated as 36*4/3 = 48 %. The measured oPs ratio is, however, significantly lower than the value reported by Petkov et al. for porous MSSQ films [3].

While the 3 γ annihilation fraction measurements yield indirect evidence for positronium emission from the porous films into vacuum, time-of-flight studies can not only prove the emission but also measure the energy of the emitted oPs. On Fig. 3 the oPs TOF peak is shown at 3 keV positron beam energy in 15 mm distance from the surface of the "C" film grown with 0.22 molar ration CTACl (C 0.22 sample). At this energy value the 3 γ signal is still at approximately 90 % of the maximum, suggesting an efficient oPs emission. The implantation depth is sufficient to expect efficient thermalization of the oPs in the pore system. By comparing the TOF curve with model spectra calculated using the Monte-Carlo code GEANT 4 [13], oPs emission with an energy of 86 meV corresponds well to the measured curve. The model expects monoenergetic positronium and isotropic angular distribution, therefore the energy value should be treated as an approximation. Similar oPs emission energy was found in the F 0.016 sample as well. Although the absolute positronium reemission probability could not be determined from the TOF spectra alone, the F and C films proved to convert positron into positronium with similar efficiency, as the 3 γ annihilation fraction measurement suggested already. This similarity suggests that most of the oPs that is detected in the 3 γ measurement leave the sample, giving a positron/orthopositronium conversion efficiency of nearly 30 % for the mesoporous layers.

Conclusions

Positron studies using a variable energy beam found similar 3 γ annihilation fraction (30-36 %) in porous silica layers with very different pore size and structure. The signal can be

attributed to orthopositronium emission from the layers, showing open porosity. The 300-700 nm thick mesoporous films emit oPs with nearly 100 meV energy, complete thermalization of orthopositronium has not been reached. TOF measurements are planned to check if increased layer thickness, cooling of the film or a change of the pore surface groups lead to more efficient orthopositronium slowing down.

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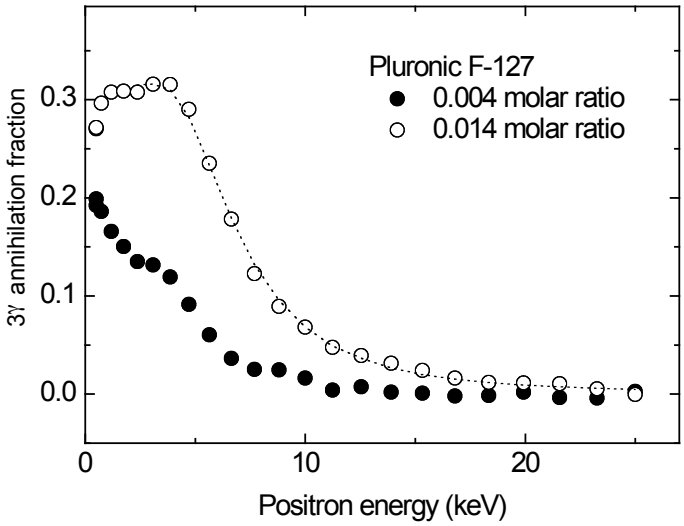

Figure 1
3 γ annihilation fraction as a function of the positron beam energy in samples grown using F-127 as template with two different molar ratio.

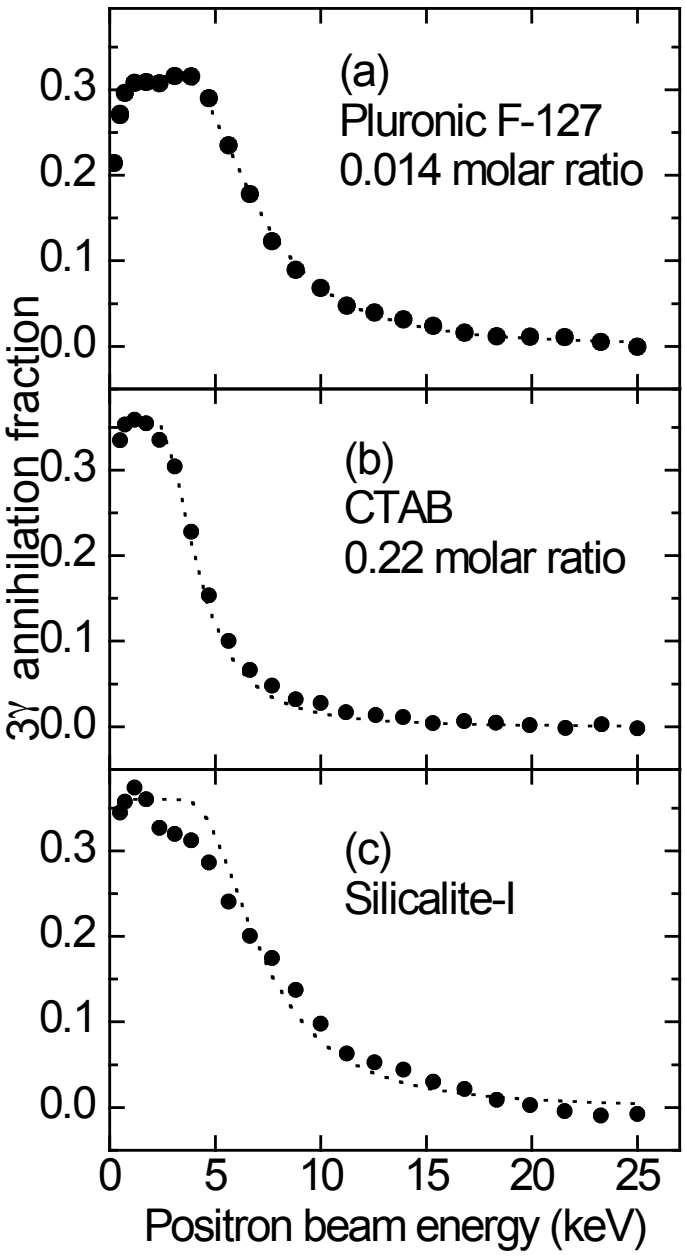

Figure 2
3 γ annihilation fraction as a function of the positron beam energy in porous silica layers grown using Pluronic F 128 (a), CTACl (b) as porogen and in thin silicalite-I layer (c) deposited on glass. The dotted line represents a simple model assuming no positron or oPs diffusion.

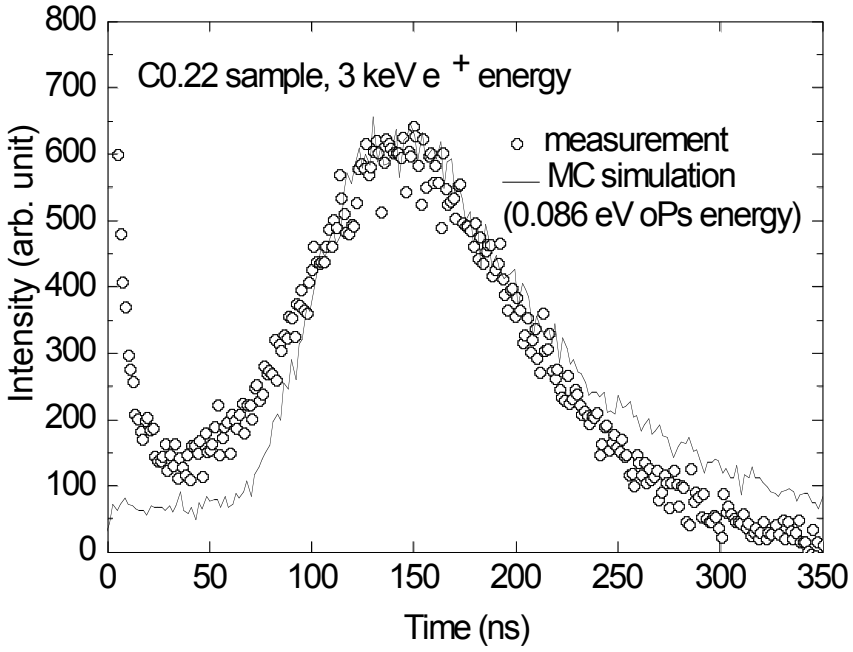

Figure 3
Time-of flight spectrum of a thin porous silica layer grown using CTACl in 0.22 CTACl/Si molar ratio at 3 keV positron beam energy and 15 mm distance. The continuous line is a Monte-Carlo simulation of the measurement assuming oPs emission into the vacuum with 0.086 eV energy.